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(54) Catalyst for purifying exhaust gas and method for purifying exhaust gas with the catalyst

(57) The present invention provides a catalyst for purifying an exhaust gas having excellent heat resistance and a small level of deterioration of the purifying ability of the exhaust gas even if the catalyst is exposed to a high temperature atmosphere for a long time. The catalyst for purifying an exhaust gas comprises a catalytic metal for oxidizing HC and CO and reducing NO_x for purification, and a mixed oxide containing Ce, Zr and Sr.

EP 1 127 603 A1

INSDOCID: <EP 1127603A1 | >

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a catalyst for purifying an exhaust gas and a method for purifying an exhaust gas with the catalyst.

[0002] Three way catalysts, which can purify HC (hydrocarbon), CO and NO_x simultaneously in an exhaust gas in the vicinity of the theoretical air-fuel ratio very effectively, are known as a catalyst for purifying an exhaust gas from an engine. Also known is a so-called lean NO_x purifying catalyst, which is as follows. At a lean air-fuel ratio, NO_x contained in the exhaust gas is stored in a NO_x storage material such as Ba, and at the theoretical air-fuel or a rich air-fuel ratio, the stored NO_x is migrated onto a precious metal and is reacted with a reducing gas such as HC, CO and H_2 contained in the exhaust gas to reduce NO_x to N_2 for purification, and to oxidize and purify the reducing gases at the same time.

[0003] Generally, these catalysts contain an oxygen storage material that stores and releases oxygen by changing the oxidation number, and CeO_2 or a $CeO_2 \cdot ZrO_2$ mixed oxide is commonly used as the oxygen storage material. In the three way catalysts, these oxides serve to correct a deviation from the theoretical air-fuel ratio by storing or releasing oxygen. In the lean NO_x purifying catalyst, these oxides serve as an oxygen supply source for oxidizing a large amount of NO contained in an exhaust gas to NO_2, which can easily be stored in the NO_x storage material.

[0004] Japanese Patent Laid-Open Publication NO.6-315634 discloses a catalytic structure for nitrogen-oxygen catalytic reduction comprising a carrier, an inner layer on the carrier and a surface layer on the inner layer, the inner layer comprising a catalytic component expressed by a general formula $A_xB_{1-x}CO_3$, (where A is at least one element selected from the group consisting of La, Y, Ce and the like, B is at least one element selected from the group consisting of Na, K, Sr and the like, and C is at least one element selected from the group consisting of Mn, Co, Zr and the like, and $0 \leqq X \leqq 1$), the surface layer comprising a catalyst component where an active component comprising an oxide of an element of Group Ib, IIa or IIb of the periodic table is supported by a support such as aluminum oxide, titanium dioxide, and zirconium oxide. In this catalytic structure, hydrocarbon is adsorbed by the surface layer for activation, whereas a nitrogen oxide is adsorbed onto the inner layer for activation, so that the activated hydrocarbon and the activated nitrogen oxide are reacted at the interface therebetween. High activity and selectivity for reduction of the nitrogen oxide are expected from this structure.

[0005] However, when a catalyst is exposed to a high temperature atmosphere for a long time, an oxide constituting the oxygen storage material is deteriorated, so that oxygen is not stored or released properly. As a result, the performance of the catalyst for purifying an exhaust gas is deteriorated.

[0006] The object of the present invention is to provide a catalyst for purifying an exhaust gas whose performance for purifying an exhaust gas is not significantly deteriorated at exposure to a high temperature atmosphere for a long time and that has excellent heat resistance.

[0007] Another object of the present invention is to improve the sulfur poisoning resistance and the regeneration properties from sulfur poisoning.

[0008] Furthermore, another object of the present invention is to provide a method for purifying an exhaust gas using such a catalyst.

SUMMARY OF THE INVENTION

[0009] The present invention uses a Ce-Zr-Sr mixed oxide containing Ce, Zr and Sr as constituent elements (which may be referred to as a $CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide in the following description).

[0010] A catalyst for purifying an exhaust gas of the present invention includes a catalytic metal that serves for oxidation of HC and CO in the exhaust gas containing oxygen and reduction of NO_x in the exhaust gas, and a mixed oxide comprising Ce, Zr and Sr.

[0011] According to this embodiment, the mixed oxide that acts as an oxygen storage material contains Sr in addition to Ce and Zr, so that the oxygen storage function of the catalyst is not significantly deteriorated even if the catalyst is exposed to a high temperature atmosphere for a long time. Moreover, a catalyst having an excellent heat resistance can be obtained. The reason for this is not clear, but it may be as follows.

[0012] An analysis indicates that when a Ce-Zr mixed oxide ($CeO_2 \cdot ZrO_2$ mixed oxide) is heated, ZrO_2 is separated. However, in a Ce-Zr-Sr mixed oxide, such separation of ZrO_2 hardly occurs, and the Ce-Zr-Sr mixed oxide is highly crystalline. Therefore, even if it is exposed to a high temperature, it hardly is degraded so that the oxygen storage function is not deteriorated. It seems that Sr contributes to this high crystallinity.

[0013] An analysis indicates that since the primary particles of the Ce-Zr-Sr mixed oxide have a small particle size, it is difficult that sintering due to heat proceeds. It seems that Sr contributes to the fact that the particles are fine.

[0014] An analysis indicates that since the secondary particles of the Ce-Zr-Sr mixed oxide have a large particle size, mesopore is also large which makes it easy that the exhaust gas is diffused to the inside. This advantageously

SDOCID: <EP 1127603A1 >

serves for storage and release of oxygen, and therefore high oxygen storage ability can be exerted at a relatively high temperature as well. Furthermore, it seems that the fact that Sr activates oxygen advantageously serves for storage and release of oxygen.

[0015] Therefore, the catalyst of the present invention can be provided at an exhaust pipe in which the temperature of the catalyst is constantly or temporarily at 700°C or more or in a place where the temperature of the catalyst is at 800°C or more, or at further higher 900 °C or more, such as a site immediate downstream of an exhaust manihold.

[0016] Furthermore, when the present invention is used to a ternary catalyst, even if the catalyst is exposed to a high temperature atmosphere for a long time, the mixed oxide effectively can function as the oxygen storage material that corrects a deviation of the air-fuel ratio from the theoretical air-fuel ratio by storage and release of oxygen. Thus, high HC purification performance can be obtained.

[0017] When the present invention is used as a lean NO_x purifying catalyst, even if the catalyst is exposed to a high temperature atmosphere for a long time, the mixed oxide effectively can function as the supply source that supplies oxygen having high activity for oxidation of NO. Thus, at a lean air-fuel ratio, NO is oxidized to NO_2, which is readily stored by the NO_x storage material, so that high lean NO_x purification performance can be obtained.

[0018] NO_x storage materials have a problem of so-called sulfur poisoning that deprives a NO_x storage material of its function as a NO_x storage material, because of its formation of a salt by reacting with a sulfur oxide contained in exhaust gases. However, the Ce-Zr-Sr mixed oxide makes it possible that deterioration of the lean NO_x purification performance due to sulfur poisoning can be suppressed to a small level, and provides a catalyst having excellent sulfur poisoning resistance. The reason for this is not clear, but it seems that the presence of Sr provides fine particles of the NO_x storage materials and the surface area of the NO_x storage materials becomes large, so that the NO_x storage materials are unsusceptible to sulfur poisoning. In addition, the catalyst can be regenerated by raising the temperature of the sulfur-poisoned catalyst, and in the catalyst of this embodiment, the Ce-Zr-Sr mixed oxide has high heat resistance so that very high regeneration performance can be obtained.

[0019] The Ce-Zr-Sr mixed oxide is advantageous for sulfur poisoning resistance when the content of Zr becomes large, and the heat resistance thereof is improved when the content of Ce becomes large. However, the content of Sr is too excessive, the heat resistance is deteriorated.

[0020] In the Ce-Zr-Sr mixed oxide, the amount of released oxygen is not very large when the air-fuel ratio of the engine is the stoichiometric or rich ratio at a regular temperature of the exhaust gas of around 350°C. Therefore, the period of time during which the air-fuel ratio is kept stoichiometric or rich to release NO_x absorbed in the NO_x storage materials for reduction and purification can be shortened, or the degree of the rich ratio can be reduced.

[0021] More specifically, when the amount of released oxygen is large, even if the reduction components (HC, CO, H_2, etc.) in the exhaust gas for purification of NO_x is made large by making the air-fuel ratio stoichiometric or rich, the amount of the reduction components consumed by reaction with the released oxygen also becomes large. Therefore, a larger amount of reduction components is required for reduction and purification of NO_x. In other words, it is necessary to prolong the period of time during which the air-fuel ratio is kept stoichiometric or rich or to raise the degree of the rich ratio. On the other hand, the Ce-Zr-Sr mixed oxide has a small amount of released oxygen, so that the amount of consumed reduction components is small. Therefore, the period of time during which the air-fuel ratio is kept stoichiometric or rich for reduction and purification of NO_x can be shortened, or the degree of the rich ratio can be reduced. Consequently, the amount of fuel consumption for the stoichiometric or rich air-fuel ratio can be reduced.

[0022] A method for producing the Ce-Zr-Sr mixed oxide may be, but not limited to, coprecipitation in which alkali is dropped to a mixed aqueous solution comprising salts of Ce, Zr and Sr dissolved to precipitate a mixed oxide; a solid phase reaction in which a mixture of particles of oxides of Ce, Zr and Sr is melted at a high temperature to produce a mixed oxide; evaporation to dryness in which an aqueous solution containing ions of one or two metals of Ce, Zr and Sr is prepared, oxide powder of the remaining metal of Ce, Zr and Sr is placed in the aqueous solution, the aqueous solution is stirred, and the aqueous solution is dried and calcined to form a mixed oxide; a method for obtaining crystals of a mixed oxide by boiling a mixed solution comprising salts of Ce, Zr and Sr dissolved to remove water; or the like.

[0023] When a precious metal is used as the catalytic metal, activated oxygen is supplied from the mixed oxide, and NO_x and HC in the exhaust gas can be activated on the surface of the precious metal. Therefore, an oxidation reaction of NO in the exhaust gas to NO_2, and partial oxidation reaction of HC proceeds smoothly. Since NO_2 and the partially oxidized HC are highly reactive in terms of energy, reduction of NO_x and oxidation of HC proceed efficiently.

[0024] The catalyst of the present invention can contain a NO_x storage material that absorbs NO_x in the exhaust gas in an oxygen-excessive atmosphere in which an oxygen concentration in the exhaust gas is high (lean air-fuel ratio), and releases the absorbed NO_x by reduction of the oxygen concentration (rich air-fuel ratio). Thus, the catalyst can act as a so-called lean NO_x purifying catalyst. In this case, as described above, the mixed oxide effectively can function as a supply source that supplies oxygen for oxidation of NO, even if the catalyst is exposed to a high temperature atmosphere for a long time. Therefore, the present invention provides high lean NO_x purification performance by oxidizing NO to NO_2 and absorbing the NO_2 in the NO_x storage materials at a lean air-fuel ratio.

[0025] A specific embodiment of such a lean NO_x purifying catalyst includes a carrier; an inner catalytic layer disposed

NSDOCID: <EP 1127603A1 I >

on the carrier containing a precious metal, a NO_x storage material and the Ce-Zr-Sr mixed oxide; and an outer catalytic layer disposed on the inner catalytic layer containing a precious metal and zeolite, the inner catalytic layer and the outer catalytic layer being laminated on the carrier in this order.

[0026] According to this embodiment, at a lean air-fuel ratio, in the outer catalytic layer, HC that has been stored in zeolite is released and reacted with NO in the exhaust gas for purification of NO_x. In the inner catalytic layer, NO_2 generated by oxidation of NO in the outer catalytic layer is stored in the NO_x storage materials, and apparently NO_x is purified. NO_2 stored in the NO_x storage materials is reacted with activated partially oxidized HC on the precious metals of the outer catalytic layer when the air-fuel ratio is turned to be rich so that NO_2 is degraded and purified. These effects of the two layers are combined so that very high lean NO_x purification performance can be exhibited. Therefore, the outer catalytic layer exerts a function as a catalyst for selective reduction NO_x purification, and the inner catalytic layer exerts a function as a catalyst for lean reduction NO_x purification.

[0027] As the NO_x storage material, it is preferable to use a combination of Ba, K, Sr, and Mg. Thus, deterioration of the NO_x absorption ability of the NO_x storage material due to sulfur poisoning can be suppressed. Moreover, the heat resistance of the NO_x storage material can be improved. The reason for this is not clear, but it seems as follows.

[0028] First, it seems that the elements (K, Sr, Mg) other than Ba are more susceptible to sulfur poisoning than Ba, so that the degree of sulfur poisoning of Ba is made relatively small. More specifically, Ba has higher NO_x absorption ability than those of the other elements, but the presence of the other elements makes the degree of sulfur poisoning of Ba relatively small. Therefore, the degree of decrease of the NO_x absorption ability is small.

[0029] According to an analysis, it appears that Ba and Sr (at least a part of each of them) form a compound (a mixed oxide or a double salt) constituted by these two elements. It seems that such a Ba-Sr compound is less susceptible to sulfur poisoning than Ba alone, so that deterioration of the NO_x absorption ability can be suppressed.

[0030] According to an analysis, it appears that Ba and Mg (at least a part of each of them) come close to each other or are combined to be nearly amorphous, although it is not crystalline. Such a Ba-Mg coexisting substance suppresses sulfur poisoning of Ba (production of barium sulfate) more than in the case of Ba alone, so that deterioration of the NO_x absorption ability can be suppressed.

[0031] According to an analysis, it appears that K is not combined with or not be compatible with Ba, Sr or Mg, and is dispersed around the Ba-Sr compound or the Ba-Mg coexisting substance. It seems that since K is relatively highly reactive with sulfur, K prevents the Ba-Sr compound or the Ba-Mg coexisting substance from being sulfur-poisoned. Furthermore, K facilitates crystallinity of the Ba-Sr double carbonate, and activates the NO_x storage material. Therefore, K contributes to improvement of the heat resistance of the catalyst.

[0032] It seems that the quaternary material of Ba-K-Sr-Mg as the NO_x storage material has weakened bonding to SO_x because of an interaction between the four elements, so that even if SO_x binds thereto, it can be detached readily.

[0033] When Ba is an only element constituting the NO_x storage material and the amount thereof is increased, only the particle size is increased, and the specific surface area is not significantly increased. However, when Ba is combined with the other elements (K, Sr, Mg) and the amount thereof is increased, the particle size is not significantly increased, and the specific surface area or the active site is increased. Therefore, it seems that the volume of absorbed NO_x and SO_x is increased. Therefore, even if more or less sulfur poisoning occurs, the NO_x absorption ability is not significantly deteriorated.

[0034] As described above, the combination of Ba and the other elements (K, Sr, Mg) is advantageous to provide fine particles of the NO_x storage materials. In particular, Sr has a significant function to make Ba and Mg particles fine. Thus, high dispersibility on the support of the NO_x storage materials can be achieved, and heat sintering hardly occurs. In other words, the heat resistance of the catalyst can be high.

[0035] When the Ce-Zr-Sr mixed oxide and alumina are used together as the NO_x storage material and the support material of the precious metal, the heat deterioration of the catalyst advantageously can be prevented, because the alumina hardly is sintered or broken even at a high temperature. However, in the case of alumina, when the catalyst has a high temperature, Ba is reacted with the support and this facilitates deterioration. On the other hand, Mg serves to suppress the reaction of the support and Ba and prevents the heat deterioration of the catalyst.

[0036] As the alumina, for a ternary catalyst, an addition alumina added with Ba, Zr, La, or the like to suppress reduction of the specific surface area when the catalyst is exposed to high temperatures may be used. However, it is advantageous to use a non-addition alumina that does not contain these additional elements for NO_x purification at a lean ratio. More specifically, at a lean ratio, the precious metal acts as a catalyst for oxidizing NO in the exhaust gas to NO_2, and assists the absorption of NO_x by the NO_x storage materials. The alumina serves to assist the catalytic reaction of the precious metal. When an additive as described above is present, the function of the alumina as a cocatalyst is deteriorated, although the heat resistance is improved. Therefore, a non-addition alumina is advantageous for NO_x purification at a lean ratio.

[0037] It is preferable to combine alumina and a Ce-Zr-Sr mixed oxide at a mass ratio of 1:1 or more or less 1:1. This is advantageous for both improvement of the heat resistance of the catalyst and improvement of the sulfur poisoning resistance.

[0038] As the precious metal, it is preferable to use Pt, which has a high catalytic function for oxidation of NO to NO_2 at a lean ratio and reduction of NO_2 to N_2 at the stoichiometric or rich ratio. It is more preferable to use both Pt and Rh. Rh serves to assist a catalytic reaction of Pt, namely, promotes the ternary reaction described above at the stoichiometric or rich ratio, and promotes a reduction and degradation reaction of NO_x released from the NO_x storage material. When the Rh support amount per L of the carrier is in the range from about 0.1 to 1.0g, the Rh support amount does not significantly affect the NO_x purification ratio. Therefore, the Rh support amount can be small.

[0039] It is preferable that the Pt support amount per L of the carrier is 1 to 15g. Amounts of less than 1g do not allow sufficient reduction and purification. Amounts of more than 15g provide no improvement in the NO_x purification ratio, leading to high cost. The Rh support amount is preferably, for example, about 1/10 to 1/100 of the Pt support amount.

[0040] In the catalyst for purifying an exhaust gas, the support amount of Sr as the NO_x storage material per L of the carrier is preferably 8 to 20g, and the support amount of Mg per L of the carrier is preferably 5 to 15g, more preferably, 8 to 12g.

[0041] Thus, the effect of Mg on improvement of the heat resistance can be obtained, and at the same time, the effect of Mg and Sr on improvement of the sulfur poisoning resistance can be obtained. The Ba support amount per L of the carrier is 25 to 60g.

[0042] In the catalyst for purifying an exhaust gas, the mass ratio of Ba, Sr and Mg in the catalytic layer is preferably Ba : Sr : Mg = 30 : (8 to 20) : (8 to 12).

[0043] This is advantageous for improvement of the heat resistance of the NO_x storage material while suppressing the sulfur poisoning of the NO_x storage material.

[0044] In the catalyst for purifying an exhaust gas, the mass ratio of Ba, K, Sr and Mg in the catalytic layer is preferably Ba : K : Sr : Mg = 30 : (2 to 12) : (8 to 20) : (8 to 12).

[0045] This is advantageous for improvement of the heat resistance of the NO_x storage material while suppressing the sulfur poisoning of the NO_x storage material.

[0046] In the catalyst for purifying an exhaust gas, the support amount of K per L of the carrier is preferably 2 to 12g.

[0047] More specifically, promotion of the crystallinity of the Ba-Sr double carbonate by K and the resulting improvement of the heat resistance of the catalyst can be achieved when the K support amount is 2g/L or more. However, when the K support amount exceeds 12g/L, the effects are weakened. In this case, the K support amount is more preferably 4 to 10g/L.

[0048] In the catalyst for purifying an exhaust gas, the support amount of K per L of the carrier is preferably 2 to 6g.

[0049] More specifically, since the support amount of K per L of the carrier is 6g or less in the present invention, deterioration of the oxidation and purification ability of HC due to the precious metal can be suppressed when the oxygen concentration in the exhaust gas decreases after exposed to a high temperature atmosphere (when an atmosphere with reductants ($\lambda \leqq 1$) is reached).

[0050] Since the support amount of K per L of the carrier is 2g or more in the present invention, the effect of K on preventing sulfur poisoning of Ba, Mg and Sr can be obtained, and NO_x released from the NO_x storage material can be reacted with HC sufficiently for purification when switching a lean combustion operation to a theoretical air-fuel ratio combustion operation or a rich combustion operation.

[0051] When the support amount of K per L of the carrier is 2g to 6g, the mass ratio of Ba and K in the catalytic layer is preferably Ba : K = (5 to 15) : 1.

[0052] More specifically, since the mass ratio of the Ba support amount to the K support amount is 5 or more, the NO_x absorption ability never becomes insufficient, which might occur when the Ba support amount is small. Since this mass ratio is 15 or less, the NO_x absorption site of Ba never decreases, which might be caused by sintering during catalyst calcining because the Ba support amount is large. Moreover, there is no occurrence of detachment of Ba as a result of crystallization of Ba on the support.

[0053] Therefore, when the oxygen concentration in the exhaust gas is high (during lean combustion operation of the engine), the NO_x absorption properties of Ba are not deteriorated. When the oxygen concentration in the exhaust gas becomes low (during theoretical air-fuel ratio combustion or rich combustion operation of the engine), the NO_x released from Ba can be reacted with HC sufficiently. Thus, such a function can be performed more properly.

[0054] In the catalyst for purifying an exhaust gas, "when the oxygen concentration in the exhaust gas is high" refers to, for example, when the oxygen concentration is at least 5%.

[0055] In the catalyst for purifying an exhaust gas, the engine can be a gasoline engine for lean burning or a diesel engine.

[0056] The catalyst for purifying an exhaust gas that is provided in the passage of exhaust gases from the engine and reduces the NO_x concentration in the exhaust gas containing NO_x, sulfur and oxygen can be produced by a method comprising the steps of:

coating a carrier with a Ce-Zr-Sr mixed oxide and alumina as a support; and
impregnating the coating layer with a Ba solution, a K solution, a Sr solution, a Mg solution and a solution of a

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precious metal.

[0057] This embodiment provides a catalyst for purifying an exhaust gas comprising a carrier and a catalytic layer on the carrier, the catalytic layer comprising Ba, K, Sr and Mg as NO_x storage materials and a precious metal for reducing NO_x that are supported on a support (Ce-Zr-Sr mixed oxide and alumina). Thus, the heat resistance of the NO_x storage material can be improved while suppressing sulfur poisoning of the NO_x storage materials.

[0058] In the method for producing the catalyst for purifying an exhaust gas, all of the Ba solution, the K solution, the Sr solution, and the Mg solution are preferably acetate solutions.

[0059] In the method for producing the catalyst for purifying an exhaust gas, it is preferable to form the coating layer in the form of a multiple layer by coating the carrier with the support by two operations, and then impregnating the two layers with the Ba solution, the K solution, the Sr solution, the Mg solution, and the precious metal solution.

[0060] More specifically, in forming a thick catalytic layer on a carrier, when the carrier is coated with the support by one operation, the thickness of the support layer tends to be non-uniform because the amount of the support is large. In addition, drying and calcining of the support layer takes a long time. On the other hand, coating by two operations, as described above, is advantageous for achieving a uniform thickness of the support layer, and time for drying and calcining can be shortened. Furthermore, when the support layer is constituted by two layers, and the support layer is impregnated with the NO_x storage materials, the concentration of the NO_x storage materials in the outer support layer is higher than that of the inner support layer. Therefore, SO_x is trapped primarily by the NO_x storage materials of the outer support layer, and this ensures that the inner support layer can be provided with the NO_x storage materials that are sulfur-poisoned only in a small level. This is advantageous for maintaining the NO_x purification performance.

[0061] In the method for producing the catalyst for purifying an exhaust gas, it is preferable to mix the Ba solution, the K solution, the Sr solution, the Mg solution and the solution of a precious metal so that the support is impregnated with the solutions simultaneously.

[0062] More specifically, when the solution of a precious metal solution and the solution of the NO_x storage materials are separated and the support is impregnated with the solution of a precious metal first, the precious metal is covered by the NO_x storage materials used later for impregnation, and tends to be buried therein. On the other hand, when the support is impregnated with the solution of a precious metal later, the NO_x storage materials, especially Ba, are eluded in the solution of a precious metal so that the dispersibility becomes poor.

[0063] On the other hand, simultaneous impregnation allows the precious metal to be arranged close to the NO_x storage materials without the precious metal being buried. In addition, simultaneous impregnation does not lead to poor dispersibility of Ba, so that this is advantageous for NO_x reduction and purification. Furthermore, simultaneous impregnation of four kinds of NO_x storage material solutions efficiently forms the Ba-Sr compound and the Ba-Mg coexisting substance and allows K to be dispersed around them. This is advantageous for suppressing sulfur poisoning of the NO_x storage materials, and for providing fine particles of the NO_x storage materials, in particular, fine particles of Ba and Mg provided by an action of Sr. Thus, the heat resistance of the catalyst becomes high.

[0064] In the method for producing the catalyst for purifying an exhaust gas, when the Ba solution, the K solution, the Sr solution, the Mg solution are divided into two groups, one for the earlier impregnation of the support layer and one for the later impregnation, it is preferable to use the K solution in the later impregnation.

[0065] More specifically, in the case where the Ba solution, the K solution, the Sr solution, and the Mg solution are used to impregnate the support simultaneously, when the amounts of Ba, K, Sr and Mg to be supported are large, the concentrations of the metals in the impregnation solution become high, and therefore for example Ba, which has a low solubility, remains in the impregnation solution without being dissolved. In this case, in the metal components are non-uniform in impregnation, so that the catalyst performance may be reduced.

[0066] On the other hand, if the impregnation solution is heated, the solubility is increased so that all the metal components can be dissolved without increasing the total amount of the impregnation solution. However, the heating process is required. Therefore, it is preferable that the Ba solution, the K solution, the Sr solution, the Mg solution are divided into two groups, one for the earlier impregnation of the support and one for the later impregnation, and the K solution is used in the later impregnation.

[0067] In this case, since K is not combined with or not compatible with the other NO_x storage materials, it is not necessary to use the K solution for impregnation at the same time with the other NO_x storage materials. On the contrary, using the K solution in the later impregnation is advantageous

[0068] In the method for producing the catalyst for purifying an exhaust gas, when the Ba solution, the K solution, the Sr solution, the Mg solution are divided into two groups, one for the earlier impregnation of the support and one for the later impregnation, it is preferable to use the Sr solution in the earlier impregnation.

[0069] More specifically, since it seems that Sr serves to make the particles of Ba and Mg fine, the particles of Ba and Mg are made fine by Sr being supported earlier, which is advantageous for enhancing the heat resistance of the catalyst.

[0070] Furthermore, an apparatus for purifying an exhaust gas can be constructed as shown in Figure 1. More spe-

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cifically, the apparatus includes:

a catalyst **25** for purifying an exhaust gas provided in a passage **22** for an exhaust gas from an engine **1** or the like, comprising a NO_x storage material that absorbs NO_x and a sulfur component in the exhaust gas in an oxygen-excessive atmosphere in which an oxygen concentration in the exhaust gas is high, and releases the absorbed NO_x by reduction of the oxygen concentration;
sulfur-excessive absorption determining means ***a*** for determining a excessive absorption state of the sulfur component in the NO_x storage material; and
sulfur detaching means ***b*** for detaching the sulfur component from the NO_x storage material by raising the temperature of the catalyst 25 and lowering the concentration of oxygen, when the sulfur-excessive absorption determining means ***a*** determines that the absorption of the sulfur component is in an excessive state.

wherein the NO_x storage material is constituted by Ba and at least one element selected from the group consisting of K, Sr, Mg and La.

[0071] In such an embodiment, the sulfur detaching means ***b*** is operated after the sulfur component (SO_x) in the exhaust gas has been absorbed in the NO_x storage material excessively. This embodiment makes it easy to regenerate the NO_x storage material almost to the NO_x absorption ability before the sulfur component is absorbed. In other words, the NO_x absorption ability of the NO_x storage materials after regeneration (which means regeneration from sulfur poisoning, which also applies to the following) is higher than that the NO_x storage material comprising Ba alone, or the degree of deterioration of the NO_x absorption ability when exposed to a high temperature is smaller. In other words, the heat resistance is higher. This improvement of the heat resistance is advantageous for regeneration of the NO_x storage materials. The relationship between the improvement of the heat resistance and the regeneration of the NO_x storage materials is as follows.

[0072] The sulfur detaching means ***b*** detaches the sulfur component from the NO_x storage materials not only by lowering the concentration of oxygen in the exhaust gas, but also by raising the temperature of the catalyst **25**. Therefore, for a catalyst comprising NO_x storage materials having a low heat resistance, it is difficult to raise the temperature of the NO_x storage materials to detach the sulfur component, which prevents achievement of the original object of the present invention. On the other hand, as in the present invention, when the heat resistance of the NO_x storage materials is high, the sulfur detaching means ***b*** can be effectively used for regeneration of the NO_x absorption ability. In other words, deterioration of the NO_x storage materials due to heat during sulfur detaching treatment can be avoided.

[0073] Thus, the NO_x absorption ability after regeneration is higher than that the NO_x storage material comprising Ba alone, or the heat resistance is higher. The reason for this is not clear, but it seems to be as follows.

[0074] First, it seems that the elements (K, Sr, Mg or La) other than Ba are more susceptible to sulfur poisoning than Ba, so that the degree of sulfur poisoning of Ba is made relatively small. Therefore, the degree of a decrease of the NO_x absorption ability after sulfur poisoning is small. More specifically, Ba has higher NO_x absorption ability than those of the other elements, but the presence of the other elements makes the degree of sulfur poisoning of Ba relatively small. Therefore, the degree of decrease of the NO_x absorption ability is small.

[0075] Furthermore, it seems that the elements (K, Sr, Mg or La) other than Ba are more readily to be regenerated from sulfur poisoning than Ba, so that the NO_x absorption ability after regeneration is higher. In other words, a sulfate in which Ba is combined with SO_x is stable. However, sulfates of the other elements is unstable compared with the sulfate of Ba, and therefore, SO_x can be easily detached in an atmosphere at a high temperature and a low oxygen concentration.

[0076] Furthermore, it seems that Ba is combined with the other elements (Sr, Mg or La) except K (forming a mixed oxide or a double salt, or being close or binding to each other to be nearly amorphous), which makes it difficult for sulfur poisoning to occur.

[0077] Furthermore, when the NO_x storage material is constituted only by Ba, and the amount thereof is increased, the NO_x absorption ability before sulfur poisoning and after regeneration is not significantly improved. This seems to be because when the amount of Ba exceeds a certain amount, only the particle size is increased, and the specific surface area is not increased. However, when Ba is combined with the other elements (at least one selected from K, Sr, Mg and La), each is present separately because of the difference in the nature between the elements, and the specific surface area or the active site is increased. In addition, sintering due to heat hardly occurs. Furthermore, the interaction between the different elements constituting the NO_x storage materials facilitate the detachment of the sulfur component.

[0078] As described above, the combination of Ba and the other elements (at least one selected from K, Sr, Mg and La) is advantageous to provide fine particles of the NO_x storage materials. In particular, Sr has a significant function to make Ba and Mg particles fine. Thus, high dispersibility on the support of the NO_x storage materials can be achieved, and heat sintering hardly occurs. In other words, the heat resistance of the catalyst can be high.

[0079] When the support is alumina, Ba is reacted with the support when the catalyst reaches at a high temperature,

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which is likely to lead to deterioration. However, Mg serves to suppress the reaction between the support and Ba, so that the heat resistance of the catalyst can be high.

[0080] When Ba and the other elements (at least one selected from K, Sr, Mg and La) is supported by a carrier having a honeycomb shape or other shapes, the Ba support amount per L of the carrier is preferably about 10 to 50g, more preferably 20 to 40g. The support amounts of the other elements are preferably equal to or less than the support amount of Ba.

[0081] The exhaust gas with excessive oxygen having a high concentration of oxygen corresponds to an exhaust gas (a concentration of oxyqen of about 4 to 20%) when the engine is operated in a lean air-fuel mixture having an air-fuel ratio A/F > 16 (in particular, A/F = 18 to 50).

[0082] It is preferable that the elements constituting the NO_x storage materials include K in addition to Ba. This achieves a high NO_x absorption ability before sulfur poisoning. Furthermore, K is not combined with Ba, but is highly reactive with sulfur, so that K is present around Ba and prevents Ba from sulfur-poisoned, and suppresses deterioration of the NO_x absorption ability due to sulfur poisoning of Ba. Furthermore, it seems that K is more readily to detach the sulfur component than Ba, so that the NO_x absorption ability after regeneration is higher. The mass ratio of Ba and K is preferably, for example, Ba : K = 30 : (1 to 30).

[0083] It is preferable that the elements constituting the NO_x storage materials include at least one selected from Sr, Mg and La, in addition to Ba and K. This is advantageous for a high heat resistance of the NO_x storage materials and prevention of heat deterioration during sulfur detachment treatment.

[0084] According to an analysis, it appears that Ba and Sr (at least a part of each of them) form a compound (a mixed oxide or a double salt) constituted by these two elements. It seems that such a Ba-Sr compound is less susceptible to sulfur poisoning than Ba alone, so that deterioration of the NO_x absorption ability can be suppressed.

[0085] According to an analysis, it appears that Ba and Mg (at least a part of each of them) come close to each other or are combined to be nearly amorphous, although it is not crystalline. Such a Ba-Mg coexisting substance suppresses sulfur poisoning of Ba more than in the case of Ba alone, so that deterioration of the NO_x absorption ability can be suppressed.

[0086] According to an analysis, it appears that K is not combined with or not be compatible with Ba, Sr or Mg, and is dispersed around the Ba-Sr compound or the Ba-Mg coexisting substance. It seems that since K is relatively highly reactive with sulfur, K prevents the Ba-Sr compound or the Ba-Mg coexisting substance from being sulfur-poisoned.

[0087] When Ba, K and Mg are used as the elements constituting the NO_x storage materials and are supported by a carrier having a honeycomb or other shapes, the Ba support amount per L of the carrier is preferably 10 to 50g, the K support amount is preferably 1g (the upper limit is 15g, for example), and the Mg support amount is preferably 3 to 17g. For the Mg support amount, an amount of 5 to 15g is more preferable, and an amount of 8 to 12 g is even more preferable. These amounts provide high heat resistance and good regeneration properties from sulfur poisoning. The mass ratio of Ba, K and Mg is preferably, for example, Ba : K : Mg = 30 : (1 to 30) : (1 to 30).

[0088] When Ba, K and Sr are used as the elements constituting the NO_x storage materials and are supported by a carrier having a honeycomb or other shapes, a preferable Ba support amount and a preferable K support amount per L of the carrier are the same as those in the Ba-K-Mg based catalyst. The Sr support amount is preferably 10 to 20g. For the Sr support amount, 13 to 17g are more preferable. These amounts provide high heat resistance and good regeneration properties from sulfur poisoning. The mass ratio of Ba, K and Sr is preferably, for example, Ba : K : Sr = 30 : (1 to 30) : (1 to 30).

[0089] It is preferable that the elements constituting the NO_x storage materials include Sr, in addition to Ba. This is advantageous for achievement of a high heat resistance of the NO_x storage materials and prevention of heat deterioration during sulfur detachment treatment.

[0090] It is preferable that the elements constituting the NO_x storage materials include at least one selected from Mg and La, in addition to Ba and Sr. This is more advantageous for achievement of a high heat resistance of the NO_x storage materials and prevention of heat deterioration during sulfur detachment treatment.

[0091] It is preferable that the elements constituting the NO_x storage materials include Mg, in addition to Ba. This is advantageous for achievement of a high heat resistance of the NO_x storage materials and prevention of heat deterioration during sulfur detachment treatment.

[0092] It is preferable that the elements constituting the NO_x storage materials include La, in addition to Ba and Mg. This is more advantageous for achievement of a high heat resistance of the NO_x storage materials and prevention of heat deterioration during sulfur detachment treatment.

[0093] Raising the temperature of the catalyst **25** by the sulfur detaching means ***b*** can be achieved by raising the temperature of the exhaust gas. For example, a temperature of the exhaust gas of 500 to 1100°C (preferably 600 to 1100°C) is preferable for detachment of sulfur from the NO_x storage materials. A heater can be provided in the catalyst **25** and can be heated. Reducing the concentration of oxygen in the exhaust gas by the sulfur detaching means ***b*** can be achieved by controlling the air-fuel ratio of the engine. For example, λ(oxygen-excessive ratio) of around 1 or not more than 1 achieves a concentration of oxygen in the exhaust gas of 0.5% or less, and further leads to an increase

EPODOC: <EP 1127603A1 1 1

in the amount of the reduction components such as HC, CO, H_2 or the like in the exhaust gas. This is advantageous for detachment of the sulfur component from the NO_x storage materials.

[0094] When a spark ignition direct injected engine is used as the engine, the sulfur detaching means ***b*** is preferably fuel injection control means that operates a fuel injection valve in such a manner that fuel is divided into at least two portions to be injected to the combustion chamber in the cylinder during a period from the start of an air-intake stroke to the end of the compression stroke. This makes it possible to raise the temperature of the catalyst **25** by raising the temperature of the exhaust gas while reducing the concentration of oxygen in the exhaust gas. If such a divisional injection is used, in particular, the concentration of CO in the exhaust gas can be increased, which is more advantageous for detachment of the sulfur component from the NO_x storage materials.

[0095] More specifically, it seems that when the NO_x storage material is Ba, SO_x is adsorbed onto the surface of barium particles in the form of a sulfate, and the barium sulfate generates barium carbonate and sulfur dioxide by the following reaction progress by supply of CO.

$$BaSO_4 + CO \rightarrow BaCO_3 + SO_2 \uparrow \text{ (coefficients omitted)}$$

[0096] Furthermore, when the CO concentration becomes high, a so-called water gas shift reaction proceeds between CO and water in the exhaust gas, thereby generating hydrogen in the reaction site of the catalyst.

$$CO + H_2O \rightarrow H_2 + CO_2$$

Then, the action of hydrogen causes the sulfur component adsorbed onto the NO_x storage material to be detached. This is advantageous for detachment of the sulfur component. Since the water gas shift reaction proceeds even in a relatively low temperature, it is not necessary to raise the temperature of the catalyst **25**.

[0097] The sulfur excessive absorption determining means that determines the excessive absorption state of the sulfur component to the NO_x storage material operates in the following manner, for example: estimating an amount of absorbed SO_x in the NO_x storage material, based on the travel distance of the automobile and the total amount of fuel consumed during that period, or further in view of the temperature of the catalyst **25** during that period, and determining that the sulfur component reaches the excessive absorption state when the estimated value exceeds a predetermined value.

[0098] Therefore, a method for purifying an exhaust gas including NO_x and a sulfur component preferably includes:

allowing a NO_x storage material comprising Ba and at least one selected from the group consisting of K, Sr, Mg and La to absorb the NO_x and the sulfur component by contacting the exhaust gas with the NO_x storage material when the exhaust gas is in an oxygen-excessive state in which an oxygen concentration is high, and
raising the temperature of the NO_x storage material and reducing the concentration of oxygen in the exhaust gas when the sulfur component absorption state of the NO_x storage material reaches a predetermined excessive absorption state, thereby detaching the sulfur component from the NO_x storage material.

[0099] As seen from the above description, such a method facilitates detachment of the sulfur component from the NO_x storage material to recover the NO_x absorption ability to a high level, when the NO_x absorption ability of the NO_x storage material is deteriorated by sulfur poisoning. Thus, this method is advantageous for purification of NO_x.

[0100] This and other advantages of the present invent ion will become apparent to those skilled in the art upon reading and understanding the following detailed description with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0101] Figure **1** is a schematic diagram illustrating a structure of an apparatus for purifying an exhaust gas according to the present invention.

[0102] Figure **2** is a schematic diagram illustrating an apparatus for purifying an exhaust gas of an embodiment of the present invention.

[0103] Figure **3** is a graph showing the output characteristics of O_2 sensor against the change in the air-fuel ratio.

[0104] Figure **4** is a cross-sectional view showing a schematic structure of a catalyst for purifying an exhaust gas according to the present invention.

[0105] Figure **5** is a graph showing an example of a map where operational regions of the stratified combustion mode, the λ = one division mode, and the enriched mode of an engine are set.

[0106] Figure **6** is a timing chart showing the combustion injection time in each operational region.

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[0107] Figure **7A** is a graph showing a map where a desired torque of an engine corresponding to the number of revolutions of the engine and the opening of the accelerator is set.

[0108] Figure **7B** is a graph showing a map where the opening of a throttle valve corresponding to the number of revolutions of the engine and the desired torque is set.

[0109] Figure **8** is a flowchart showing the basic setting procedure for the amount and the time of fuel injection.

[0110] Figure **9** is a flowchart showing a processing procedure of controlling release of NO_x.

[0111] Figure **10** is a flowchart showing a processing procedure of controlling detachment of SO_x.

[0112] Figure **11** is a flowchart showing an execution procedure of the intake stroke injection and the compression stroke injection.

[0113] Figure **12** is a flowchart showing a processing procedure of EGR control.

[0114] Figure **13** is a timing chart showing changes in the air-fuel ratio at the time of controlling NO_x release and SO_x detachment during an engine operation.

[0115] Figure **14** is a cross-sectional view illustrating a layer structure of a catalyst of an embodiment of the present invention.

[0116] Figure **15** is a block diagram of an apparatus for purifying an exhaust gas from an engine using the catalyst of an embodiment of the present invention.

[0117] Figure **16** is a graph showing the relationship between the time from the start of a test and the concentration of oxygen of a simulated gas contacted with the catalyst in measurement of the NO_x purifying ratio.

[0118] Figure **17** is a graph showing the NO_x purifying ratio for 60 seconds after switching to a lean ratio, regarding the heat resistance in Experiment **1**.

[0119] Figure **18** is a graph showing the NO_x purifying ratio for 130 seconds after switching to a lean ratio, regarding the heat resistance in Experiment **1**.

[0120] Figure **19** is a graph showing the NO_x purifying ratio for 60 seconds after switching to a lean ratio, regarding the sulfur poisoning resistance in Experiment **1**.

[0121] Figure **20** is a graph showing the NO_x purifying ratio for 130 seconds after switching to a lean ratio, regarding the sulfur poisoning resistance in Experiment **1**.

[0122] Figure **21** is a graph showing the NO_x purifying ratio for 60 seconds after switching to a lean ratio, regarding the heat resistance in Experiment **2**.

[0123] Figure **22** is a graph showing the NO_x purifying ratio for 130 seconds after switching to a lean ratio, regarding the heat resistance in Experiment **2**.

[0124] Figure **23** is a graph showing the NO_x purifying ratio for 60 seconds after switching to a lean ratio, regarding the sulfur poisoning resistance in Experiment **2**.

[0125] Figure **24** is a graph showing the NO_x purifying ratio for 130 seconds after switching to a lean ratio, regarding the sulfur poisoning resistance in Experiment **2**.

[0126] Figure **25** is a graph showing the NO_x purifying ratio for 60 seconds after switching to a lean ratio, regarding the heat resistance in Experiment **3**.

[0127] Figure **26** is a graph showing the effects of different NO_x storage materials on the NO_x purifying ratio when the catalysts are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed.

[0128] Figure **27** is a graph showing the NO_x purifying ratio of the catalysts with different NO_x storage materials at a gas temperature at the catalyst inlet of 350°C when the catalysts are fresh and after a heat deterioration treatment is performed.

[0129] Figure **28** is a graph showing the NO_x purifying ratio of the catalysts with different NO_x storage materials at a gas temperature at the catalyst inlet of 450°C when the catalysts are fresh and after a heat deterioration treatment is performed.

[0130] Figure **29** is a graph showing the effects of the Sr support amount on the NO_x purifying ratio when the catalysts are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed, regarding a catalyst with Ba-K-Sr based-NO_x storage material.

[0131] Figure **30** is a graph showing the effects of the Sr support amount on the heat resistance of a catalyst with Ba-K-Sr based-NO_x storage material.

[0132] Figure **31** is a graph showing the effects of the Mg support amount on the NO_x purifying ratio when the catalysts are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed, regarding a catalyst with Ba-K-Mg based-NO_x storage material.

[0133] Figure **32** is a graph showing the effects of the Mg support amount on the heat resistance of a catalyst with Ba-K-Mg based-NO_x storage material.

[0134] Figure **33** is a graph showing the effects of the Sr support amount on the NO_x purifying ratio, when the catalysts are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed, regarding a catalyst with Ba-K-Sr-Mg based-NO_x storage material in a Mg support amount of 5g/L.

[0135] Figure **34** is a graph showing the effects of the Sr support amount on the NO_x purifying ratio, when the catalysts

are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed, regarding a catalyst with Ba-K-Sr-Mg based-NO_x storage material in a Mg support amount of 10g/L.

[0136] Figure **35A** is a graph showing the effects of the Sr support amount on the NO_x purifying ratio, when the catalysts are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed, regarding a catalyst with Ba-K-Sr-Mg based-NO_x storage material in a Mg support amount of 15g/L.

[0137] Figure **35B** is a graph showing the effects of the Mg support amount on the NO_x purifying ratio, when the catalysts are fresh, after a sulfur poisoning treatment is performed, and after a regeneration treatment is performed, regarding a catalyst with Ba-K-Sr-Mg based-NO_x storage material in a Sr support amount of 10g/L.

[0138] Figure **36** is a graph showing the effects of the Mg support amount and the Sr support amount on the heat resistance of a catalyst with Ba-K-Sr-Mg based-NO_x storage material.

[0139] Figure **37** is a schematic model diagram showing a state of the catalytic layer of Ba-K-Sr-Mg based-NO_x storage material.

[0140] Figure **38** is a graph showing the effects of the K support amount on the sulfur poisoning resistance and the regeneration properties from the sulfur poisoning of the catalyst.

[0141] Figure **39** is a graph showing the effects of the K support amount on the heat resistance of the catalyst (the NO_x purifying ratio at a measurement temperature of 350°C).

[0142] Figure **40** is a graph showing the effects of the K support amount on the heat resistance of the catalyst (the NO_x purifying ratio at a measurement temperature of 450°C).

[0143] Figure **41** is a graph showing the relationship between the K support amount and the purifying ratio of NO_x and HC.

[0144] Figure **42** is a graph showing the relationship between the Ba support amount and the purifying ratio of NO_x.

[0145] Figure **43** is a graph showing the effects of the Pt support amount on the sulfur poisoning resistance and the regeneration properties from the sulfur poisoning of the catalyst.

[0146] Figure **44** is a graph showing the effects of the Pt support amount on the heat resistance of the catalyst (the NO_x purifying ratio at a measurement temperature of 350°C).

[0147] Figure **45** is a graph showing the effects of the Pt support amount on the heat resistance of the catalyst (the NO_x purifying ratio at a measurement temperature of 450°C).

[0148] Figure **46** is a graph showing the effects of the order of impregnation of the NO_x storage material on the sulfur poisoning resistance and the regeneration properties from the sulfur poisoning of the catalyst.

[0149] Figure **47** is a graph showing the effects of the order of impregnation of the NO_x storage material on the heat resistance of the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0150] The present invention will be described by way of example with reference to the accompanying drawings.

The overall construction of an engine

[0151] Figure **2** shows the overall construction of an engine mounted with an apparatus **A** for purifying an exhaust gas of an embodiment of the present invention. In Figure **2**, a multiple cylinder engine **1** is mounted on, for example, an automobile, and a piston **3** inserted in each cylinder defines a combustion chamber **4** in the cylinder **2**. An ignition plug **6** connected to an ignition circuit **5** is provided on the axis center of the cylinder on the upper wall of the combustion chamber **4** in such a manner that the ignition plug **6** faces the combustion chamber **4**. An injector (fuel injection valve) **7** that directly injects fuel to the combustion chamber **4** is provided on the rim of the combustion chamber **4**.

[0152] Although not shown in Figure **2**, a fuel supply circuit including a high pressure fuel pump, a pressure regulator or the like is connected to the injector **7**. The fuel supply circuit supplies fuel to the injector **7** while regulating the pressure of the fuel from a fuel tank as appropriate, and includes a fuel pressure sensor **8** for detecting the pressure of the fuel. When fuel is injected by the injector **7** in the late stage of the compression stroke of the cylinder **2**, the fuel spray is trapped in a cavity (not shown) provided on the top surface of the piston **3**, so that a layer of relatively rich air-fuel mixture is formed in the vicinity of the ignition plug **6**. On the other hand, when fuel is injected by the injector **7** in the air-intake stroke of the cylinder **2**, the fuel spray is diffused in the combustion chamber **4** and is mixed with drawn air. As a result, a homogenous air-fuel mixture is formed in the combustion chamber.

[0153] The combustion chamber **4** is in communication with an air-intake passage **10** via an air-intake port (not shown) that is opened and closed by an air-intake valve **9**. The air-intake passage **10** supplies drawn air that has been filtered with an air cleaner **11** to the combustion chamber **4** of the engine **1**, and includes a hot-wire airflow sensor **12** for detecting the amount of drawn air, an electric throttle-valve **13** for narrowing the air-intake passage **10**, and a surge tank **14** in this order from the upstream to the downstream. The electric throttle valve **13** is not mechanically coupled to an accelerator pedal (not shown), but is opened or closed by being driven by a motor **15**. Further, the throttle valve

NSDOCID: <EP 1127603A1 >

13 is provided with a throttle opening sensor **16** for detecting the opening of the throttle-valve **13**, and the surge tank **14** is provided with an air-pressure sensor **17** for detecting the pressure of the drawn air in the surge tank **14**.

[0154] The section of the air-intake passage **10** on the downstream side from the surge tank **14** is diverged into independent passages, each of which corresponds to each one of the cylinders **2**. The downstream end of each independent passage is further diverged into two passages that are in communication with the air-intake ports. One of the two diverged passages is provided with a swirl control valve **18**. The swirl control valve **18** is opened or closed by an actuator **19**. When the swirl control valve **18** opens, the air is supplied only from the other diverged passage to the combustion chamber **4**, and strong swirl of the drawn air is generated in the combustion chamber **4**. On the other hand, as the swirl control valve **4** increasingly opens, the swirl of the drawn air is weakened. Also a swirl control valve opening sensor **20** for detecting the opening of the swirl control valve **18** is provided.

[0155] In Figure **2**, an emission passage **22** for emitting burned gas from the combustion chamber **4** is diverged at the upstream end into passages, each of which corresponds to each one of the cylinders **2** and is in communication with the combustion chamber **4** via an exhaust gas valve **23** through an exhaust gas port (not shown). The emission passage **22** is provided with an O_2 sensor **24** for detecting the concentration of oxygen in an exhaust gas and a catalyst **25** for purifying the exhaust gas. The output (electromotive force) of the O_2 sensor **24** is at a reference value **E1** when the concentration of oxygen in the exhaust gas is a concentration (about 0.5%) substantially corresponding to the theoretical air-fuel ratio, as shown in Figure **3**. When the concentration is higher than that (on the rich side), the output is increased drastically, whereas the output is decreased drastically when the concentration is lower than that (on the lean side). In other words, the O_2 sensor **24** is a so-called random O_2 sensor where its output is inversed stepwise at the point of the theoretical air-fuel ratio.

[0156] The catalyst **25** is of NO_x absorption and reduction type, which absorbs NO_x in an atmosphere with excessive oxygen where the concentration of oxygen is high in the exhaust gas, and releases the absorbed NO_x when the concentration of oxygen is decreased for reduction and purification of NO_x. As shown in Figure **4**, this lean NO_x catalyst **25** has a carrier **25a** made of cordierite of honeycomb construction, and an inner catalytic layer **25b** and an outer catalytic layer **25c** on the inner catalytic layer **25b** are formed on the wall surface of each through-hole of the carrier **25a**.

[0157] The section of the emission passage **22** on the upstream side from the O_2 sensor **24** is connected to the upstream end of an EGR passage **26**, and the downstream end of the EGR passage 26 is connected to the air-intake passage **10** between the throttle-valve **13** and the surge tank **14**. An electric EGR valve **27** for regulating the opening of the passage is provided in the downstream of the EGR passage **26** so that the recirculation volume (hereinafter, referred to as EGR volume) of the exhaust gas through the EGR passage **26** can be regulated. The EGR passage **26** and the EGR valve **27** constitute exhaust gas recirculation mean. Further, a lift sensor **28** for detecting the lift amount of the EGR valve **27** is also provided.

[0158] The ignition circuit **5** of the ignition plug **6**, the injector **7**, the driving motor **15** of the electric throttle valve **13**, the actuator **19** of the swirl control valve **18**, the electric EGR valve **27** or the like are operated and controlled by a control unit **40** (hereinafter, referred to as ECU). To the ECU **40**, output signals from the airflow sensor **12**, the throttle opening sensor **16**, the air-pressure sensor **17**, the swirl control valve opening sensor **20**, the O_2 sensor **24** and the lift sensor **28** of the EGR valve **27** are input. In addition, output signals from a water-temperature sensor **30** for detecting the temperature of a coolant (engine water temperature) of the engine **1**, an air-temperature sensor **31** for detecting the temperature of the drawn air, an atmospheric pressure-sensor **32** for detecting the atmospheric pressure, an engine revolution number sensor **33** for detecting the number of revolutions of the engine, and an accelerator opening sensor **34** for detecting the opening of the accelerator pedal (the operation amount of the accelerator) are input to the ECU **40**.

General description of engine control

[0159] In the engine **1** of this embodiment, the form of fuel injection by the injector **7** (fuel injection time, air-fuel ratio or the like) can be switched depending on the operational state of the engine, so that the engine can be operated in different combustion states. In other words, for example, as shown in Figure 5, when the engine **1** is warm, a predetermined region on the side of low load and a low number of revolutions is designated as a stratified combustion region. In this region, as shown in Figure **6**, fuel is collectively injected in the late stage of the compression stroke by the injector **7**. This is a combustion mode in which combustion occurs in a stratified state where air-fuel mixture is present in the vicinity of the ignition plug **6**. In this stratified combustion mode, the opening of the throttle valve **13** is large to reduce the pump loss of the engine **1**, and thus the average air-fuel ratio in the combustion chamber **4** is significantly lean (e. g., A/F = about 30).

[0160] On the other hand, the regions for the other operations are designed to be homogenous combustion regions. In the $\lambda = 1$ division region on the low load side, fuel is injected twice by the injector **7**, namely once in the air-intake stroke and once in the compression stroke. In addition, in this region, the fuel injection quantity, the opening of the throttle or the like are controlled so that the air-fuel ratio in the combustion chamber **4** corresponds to the approximate theoretical air-fuel ratio (A/F = 14.7) (hereinafter, referred to as $\lambda = 1$ division mode). In the enriched region on the high

load and high number of revolution side in the homogenous combustion region, fuel is collectively injected in the early stage of the air-intake stroke and the air-fuel ratio is richer than the theoretical air-fuel ratio (e.g., A/F = 13 to 14) (hereinafter, referred to as an enriched mode).

[0161] In the hatched region in the control map in Figure **5**, the EGR valve **27** is opened so that part of the exhaust gas is allowed to flow back to the air-intake passage **10** through the EGR passage **26**. Although not shown in Figure **5**, when the engine is cool, all the operation regions of the engine **1** are homogenous combustion regions in order to improve the combustion stability.

[0162] More specifically, the ECU **40** determines various control parameters involved in engine outputs, based on the operation state of the engine **1**. Examples of the control parameters are the fuel injection quantity and the injection time by the injector **7**, the amount of air to be drawn that is adjusted by the throttle valve **13**, the intensity of drawn air swirl that is adjusted by the swirl control valve **18**, and the EGR amount that is adjusted by the EGR valve **27**.

[0163] More specifically, first, the desired torque **trq** of the engine **1** is calculated based on the opening of the accelerator **accel** and the number of engine revolutions **ne**. The desired torque **trq** is calculated as follows. The relationship between the opening of the accelerator **accel** and the number of engine revolutions **ne** that achieves required output performance is previously obtained by bench tests or the like. This relationship is stored in the memory of the ECU **40** as a map, and a value corresponding to the actual opening of the accelerator **accel** and the actual number of engine revolutions **ne** is read from this map. The relationship between the opening of the accelerator **accel** and the number of engine revolutions **ne** and the desired torque is as shown in Figure **7A**, for example, and the desired torque **trq** is increased with increasing the opening of the accelerator **accel** and the number of engine revolutions **ne**.

[0164] Then, an operational mode is set based on the thus obtained desired torque **trq** and the number of engine revolutions **ne**. More specifically, for example, when the engine is warm, as shown in Figure **5**, the stratified combustion mode is set when the desired torque **trq** is lower than a predetermined threshold **trq*** on the low load side, and the number of engine revolutions **ne** is small. On the other hand, in the other operation states, the homogenous combustion mode is set. Further, in this case, one of the $\lambda = 1$ division mode and the enriched mode is selected based on the desired torque **trq** and the number of engine revolutions **ne**.

[0165] Then, a desired air-fuel ratio **afw** is set for each operational mode. More specifically, in the stratified combustion mode and the enriched mode, the desired air-fuel ratio **afw** is obtained from the previously prepared map, based on the desired torque **trq** and the number of engine revolutions **ne**. In the $\lambda = 1$ division mode, the desired air-fuel ratio **afw** is set at the theoretical air-fuel ratio. Then, a desired charging efficiency **ce** is calculated based on the desired air-fuel ratio **afw**, the number of engine revolutions **ne** and the desired torque **trq**. Then, a desired throttle opening **tvo** is obtained from the previously prepared map (see Figure **7B**) based on the desired charging efficiency **ce** and the number of engine revolutions **ne**. The relationship between the number of engine revolutions and the throttle opening is varied depending on whether or not the EGR is provided. The throttle opening **tvo** is set to be larger when the EGR is provided than when the EGR is not provided.

[0166] The actual charging efficiency **ce** of the engine **1** is calculated based on the output signals from the airflow sensor **12**, and a basic fuel injection quantity **qbase** is calculated based on the actual charging efficiency **ce** and the desired air-fuel ratio **afw**.

$$qbase = KGKF \times ce/afw,$$

where KGKF is a coefficient for calculation.

At the same time, the division ratio for dividing the fuel between fuel to be injected in the air-intake stroke and fuel to be injected in the compression stroke is set for each mode. In the stratified combustion mode, the ratio for the air-intake stroke is 0%, whereas in the enriched mode, the ratio for the air-intake stroke is 100%. In the $\lambda = 1$ division mode, the division ratio is set in accordance with the desired air-fuel ratio **afw** and the number of engine revolutions **ne**.

[0167] Further, the fuel injection time is set for each operational mode. Although not shown, in the stratified combustion mode, the injection time **Inj_TT** for the compression stroke injection is obtained from the previously prepared map in accordance with the desired torque **trq** and the number of engine revolutions **ne**. On the other hand, in the homogenous combustion mode, the injection time **Inj_TL** for the air-intake stroke injection is obtained from the predetermined table in accordance with the number of engine revolutions **ne**. In the case of divided injection, the data for the stratified combustion mode is used as the injection time **Inj_TT** for the compression stroke injection, and the injection time **Inj_TL** for the air-intake stroke injection is obtained from the previously prepared map in accordance with the desired air-fuel ratio **afw** and the number of engine revolutions **ne**.

[0168] The ignition time of the engine **1** is set for each operational mode. In the stratified combustion mode, the basic ignition time is obtained based primarily on the desired torque **trq** and the number of engine revolutions **ne**. On the other hand, in the/$\lambda = 1$ division mode and the enriched mode, the basic ignition time is obtained based on the charging efficiency **ce** and the number of engine revolutions **ne**. This basic ignition time is corrected based on the engine water

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temperature. Furthermore, the swirl control valve **18** is controlled for each operational mode. In the stratified combustion mode, the opening of the swirl control valve **18** is controlled to be larger, as the desired torque **trq** is larger, or the number of engine revolutions **ne** is larger. On the other hand, in the $\lambda = 1$ division mode and the enriched mode, the opening of the swirl control valve **18** is controlled to be smaller, as the desired torque **trq** is larger, or the number of engine revolutions **ne** is larger. Also the EGR amount is controlled for each operational mode, depending on the operational state of the engine 1, which will more specifically be described later.

Constitution of the catalyst and regeneration thereof

[0169] In this embodiment, as described above, the engine **1** is in the low load region and the stratified combustion state to significantly improve the fuel efficiency, and a so-called lean NO_x catalyst **25** of absorption and reduction type is adopted so that NO_x in the exhaust gas can be reduced even if the air-fuel ratio is very lean, such as in the stratified combustion state. In order to provide the purifying performance of the catalyst **25** stably, when the amount of absorbed NO_x in the catalyst **25** is increased to some extent, the NO_x is released for reduction and purification. A slight amount of SO_x contained in the exhaust gas is gradually absorbed by a NO_x storage material, and the amount of absorbed SO_x in the catalyst **25** is gradually increased over time to a point where the increased SO_x interferes with the NO_x purifying performance. At this point, the SO_x is forcefully detached from the catalyst **25**.

[0170] The inner catalytic layer **25b** of the lean NO_x catalyst **25** includes a porous support, and a catalytic metal and a NO_x storage material that are supported by the support. Pt can be used as the catalytic metal. Ba and at least one selected from the group consisting of K, Sr, Mg and La can be used as the NO_x storage material. Alumina and a Ce-Zr-Sr mixed oxide of (or a Ce-Zr mixed oxide) can be used as the support.

[0171] Also the outer catalytic layer **25c** includes a porous support, and a catalytic metal and a NO_x storage material that are supported by the support. In this case, however, Pt and Rh can be used as the catalytic metal. Ba and at least one selected from the group consisting of K, Sr, Mg and La can be used as the NO_x storage material. Zeolite can be used as the support.

[0172] As the support of the outer catalytic layer **25c**, alumina and a Ce-Zr-Sr mixed oxide (or a Ce-Zr mixed oxide) can be used as well. Although not shown, the catalytic layer **25** can be one layer coating type, where a layer of support is formed on the surface of the wall of the carrier, and a catalytic metal and a NO_x storage material are supported by the support.

[0173] The regeneration of the catalyst **25** by detachment of NO_x and SO_x is performed when it is determined that the absorption of sulfur components by the NO_x storage material reaches the excessive absorption state. This can be achieved in the following manner. The air-fuel ratio in the combustion chamber **4** is controlled to be in the vicinity of the approximate theoretical air-fuel ratio, while the injection of fuel by the injector **7** is divided into two operations. Thus, the temperature of the exhaust gas is increased, and the temperature of the NO_x storage material is increased. At the same time, the CO concentration in the exhaust gas can be increased significantly. Furthermore, in this case, the air-fuel ratio is switched between the lean side and the rich side alternately so that the CO concentration and the HC concentration in the exhaust gas can be changed periodically.

[0174] Next, the specific process procedure of fuel injection control including the control procedure for regeneration of the catalyst **25** will be described with reference to the flowcharts shown in Figures **8** to **11**.

[0175] First, as shown in Figure **8**, in step **SA1** after the start, various kind of sensor signals such as those from the airflow sensor **12**, the O_2 sensor **24**, the water-temperature sensor **30**, the engine revolution number sensor **33**, and the accelerator opening sensor **34** are received, and various kinds of data are input from the memory of the ECU **40**. Then, in step **SA2**, the basic fuel injection quantity **qbase** is calculated and set based on the charging efficiency **ce** and the desired air-fuel ratio **afw**.

[0176] Then, in each step of steps **SA3** to **SA9**, each injection pulse width τ**L**, τ**T**, and each injection time **Inj_TL**, **Inj_TT** are obtained for each operation mode. More specifically, in step **SA3**, it is determined whether or not the operation is in the $\lambda = 1$ division mode. When the result is YES, the procedure goes to step **SA4**, and the basic fuel injection quantity **qbase** is divided between that for injection in the air-intake stroke and that for injection in the compression stroke based on the division ratio. Then, the injection pulse width τ corresponding to each injection quantity is set based on the characteristics of the injector **7** with the air-intake stroke injection pulse width τ**L** = τ**L1** and the compression stroke injection pulse width τ**T** = τ**T2**, respectively. Then, in step **SA5**, each injection time for injection in the air-intake stroke and the compression stroke is set (**Inj_TL** = **Inj_TL1**, **Inj_TT** = **Inj_TT1**).

[0177] Furthermore, in the step **SA3**, when the result of the determination is NO, that is, the operation is not in the $\lambda = 1$ division mode, the procedure goes to **SA6**, where it is determined whether or not the operation is in the stratified combustion mode. When the result is YES, the procedure goes to step **SA7**, and the air-intake stroke injection pulse width τ**L** = 0 is set, and the compression stroke injection pulse width τ**T** is set at a value τ**T1** that corresponds to the basic fuel injection quantity **qbase**. Then, in step **SA8**, the injection time for injection in the compression stroke is set (**Inj_TT** = **Inj_TT2**). On the other hand, when the result of the determination is NO in step **SA6**, that is, the operation

is not in the stratified combustion mode, the procedure goes to **SA9**, where it is determined whether or not to perform fuel cut control. When the result is YES, a return is performed, whereas when the result is NO, the procedure goes to **SA10**, where the air-intake stroke injection pulse width τ**L** is set at a value τ**T1** that corresponds to the basic fuel injection quantity **qbase**, and the compression stroke injection pulse width $\tau T = 0$ is set. Then, in step **SA11**, the injection time for injection in the air-intake stroke is set (**Inj_TL = Inj_TL3**).

[0178] Subsequently to steps **SA5**, **SA8**, and **SA11** in Figure **8**, in step **SB1** shown in Figure **9**, the amount of absorbed NO_x in the catalyst **25** is estimated. This estimation is performed based on, for example the travel distance from the point where the last instruction to release NO_x (NO_x release control) is issued and the total amount of the fuel consumed during that period. Based on the results of the estimation, in the following step **SB2**, it is determined whether or not the amount of absorbed NO_x is equal to or more than a predetermined value that has been previously set, namely, whether or not the amount of absorbed NO_x is excessive. When the result of this determination is YES, the procedure goes to **SB3**, a flag **F1** is turned to ON, which instructs NO_x release control to be performed (F1 = 1). In the step **SB2**, during acceleration of the engine **1**, the result may be YES regardless of the amount of absorbed NO_x, and the NO_x release control, which will be described below, can be performed.

[0179] Then, in step **SB4**, the first timer value **T1** whose initial value is 0 is incremented, and in the following step **SB5**, it is determined whether or not the first timer value **T1** is equal to or more than the threshold **T10** that has been previously set (approximately 2 to 10 seconds). When the result of this determination is YES, which means that the period for the NO_x release control ends, the procedure goes to steps **SB11** and **SB12**, where the flag **F1** is cleared (**F1**=0) and the first timer is reset (**T1** = 0). On the other hand, when the result of the determination in step **SB5** is NO, the procedure goes to step **SB6**, each step of steps **SB6** to **SB9**, feedback control calculation is performed based on the signals from the O_2 sensor **24**.

[0180] More specifically, in step **SB6**, an output **E** from the O_2 sensor **24** is compared with a reference value **E1** that corresponds to the theoretical air-fuel ratio. When the result is YES, which means that the output **E** is larger than the reference value **E1**, the procedure goes to **SB7**, where feedback corrected values τ**CL** and τ**CT** as current values are calculated by subtracting constants α and β, respectively, from the previous values. On the other hand, when the result is NO, which means that the output **E** is equal to or less than the reference value **E1**, the procedure goes to **SB8**, where feedback corrected values τ**CL** and τ**CT** as current values are calculated by adding constants α and β, respectively, to the previous values.

[0181] Then, in step **SB9**, the injection pulse widths τ**L** and τ**T** in the air-intake stroke and the compression stroke during NO_x release control are calculated based on the injection pulse width τ**L4** and τ**T4** obtained in accordance with the actual charging efficiency **ce** to achieve the theoretical air-fuel ratio in the combustion chamber **4** and the feedback corrected values τ**CL** and τ**CT** obtained in steps **SB7** and **SB8**, and the injection times thereof are set again.

$$\tau L = \tau L4 + \tau CL,\ Inj_TL = Inj_TL4$$

$$\tau T = \tau T4 + \tau CT,\ Inj_TT = Inj_TT4$$

[0182] In other words, during a period in which the output **E** from the O_2 sensor **24** is larger than the reference value **E1**, the air-fuel ratio is richer than the theoretical air-fuel ratio. Therefore, the fuel injection quantities in the air-intake and the compression processes are gradually decreased by constant quantities a and β for each control cycle so that the air-fuel ratio is changed to be lean. On the other hand, when the output **E** is smaller than the reference value **E1**, which means that the air-fuel ratio is lean, the fuel injection quantities are gradually increased so that the air-fuel ratio is changed to be rich. In steps **SB7** to **SB9**, the injection quantities both in the air-intake and the compression processes are feedback-corrected. However, only the injection quantity in the air-intake stroke can be feedback-corrected. This is because a change in the fuel injection quantity in the air-intake stroke hardly gives an adverse effect on the combustion state or exhaust gases.

[0183] Furthermore, in step **SB2**, when the result of the determination is NO, the procedure goes to step **SB10**, where the status of the flag **F1** is determined. When the flag is ON (**F1** = 1), which means that the NO_x release control should be performed, the procedure goes to step **SB4**. When the flag is OFF (**F1** = 0), which means that the NO_x release control should not be performed, the procedure goes to steps **SB11** and **SB12**.

[0184] Subsequently to steps **SB9** and **SB12** of Figure **9**, in step **SC1** shown in Figure **10**, the degree of sulfur poisoning of the catalyst **25**, namely, the amount of absorbed SO_x is estimated. Similarly to the estimation of the amount of absorbed NO_x in step **SB1**, this estimation is performed based on the travel distance from the point where the last instruction to detach SO_x (SO_x detachment control) is issued and the total amount of the fuel consumed during that period, in view of the temperature of the catalyst during that period. Based on the results of this estimation, in the following step **SC2**, it is determined whether or not the amount of absorbed SO_x is equal to or more than a predetermined

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value that has been previously set, namely, whether or not the amount of absorbed SO_x is excessive. At this point, the sulfur component is contained in the exhaust gas in a slight amount, so that the travel distance until the amount of absorbed SO_x becomes excessive is far longer than that until the amount of absorbed NO_x becomes excessive.

[0185] When the result of this determination in step **SC2** is YES, the procedure goes to **SC3**, a flag **F2** is turned to ON (**F2** = 1), which instructs SO_x detachment control to be performed. In the step **SC4**, the temperature of the exhaust gas **thg**, namely, the temperature of the catalyst **25**, is estimated. This estimation is performed primarily based on the actual charging efficiency **ce** and the engine revolution number **ne**, in view of the period of time for operation in the stratified combustion mode within a predetermined time before the estimation, and the time at which divided injection was performed. The temperature of the exhaust gas **thg** tends to be higher as the charging efficiency or the engine revolution number is higher, and tends to be made high by divided injection. On the other hand, in the stratified combustion mode, the temperature of the exhaust gas **thg** is significantly low, so that the temperature of the catalyst **25** becomes lower, as the period of time for operation in the stratified combustion mode is longer.

[0186] Then, in step **SC5**, it is determined whether or not the temperature of the exhaust gas **thg** is equal to or higher than the preset temperature **thg0** (e.g., 450°C). When the result of this determination is NO, the procedure goes to step **SD1** of Figure **11**. When the result of this determination is YES, the procedure goes to step **SC6**, where the SO_x detachment control is performed. In this manner, only when the temperature of the exhaust gas is high to some extent, the SO_x detachment control is performed, because the detachment properties of SO_x are not satisfactory without the temperature of the catalyst **25** being high to some extent.

[0187] In step **SC6**, the second timer value **T2** whose initial value is 0 is incremented, and in step **SC7**, it is determined whether or not the second timer value **T2** is equal to or more than the threshold **T20** that has been previously set (approximately 1 to 10 minutes). When the result of this determination is NO, the procedure goes to steps **SC8** and **SC11** and feedback control calculation is performed based on the signals from the O_2 sensor **24**. The specific procedure of the feedback control calculation is the same as that of steps **SB6** to **SB9** of Figure **9**, and therefore description thereof will be omitted. When the time corresponding to the threshold **T20** has passed and the SO_x is sufficiently detached from the catalyst **25**, the result of the determination in **SC7** becomes YES, and then the procedure goes to step **SC12**. In this step, the flag **F2** is cleared (**F2**=0) and the procedure goes to step **SD1** in Figure **11**.

[0188] On the other hand, when the result of the determination in step **SC2** is NO, the procedure goes to step **SC13** and the status of the flag **F2** is determined. When it is ON (**F2** = 1), which means that the SO_x detachment control should be performed, the procedure goes to step **SC4**. When the flag is OFF (**F2** = 0), which means that the SO_x detachment control should not be performed, the procedure goes to step **SC14** and **SC 15**. In these steps, the flag is cleared (**F2** = 0) and the second timer is reset (**T2** = 0), and the procedure goes to step **SD1**.

[0189] Subsequently to steps **SC5**, **SC12** and **SC15**, in step **SD1** shown in Figure **11**, it is determined whether or not the air-intake stroke injection pulse width τL is zero. When the result is YES ($\tau L = 0$), the procedure goes to step **SD4**. When the result is NO ($\tau L \neq 0$), the procedure goes to step **SD2**, where it is determined whether or not the timing for the air-intake stroke injection time **Inj_TL** has come. Then, the injection timing is awaited. When the injection timing has come (YES in step **SD2**), the procedure goes to step **SD3**, where the air-intake stroke injection is performed. Then, in each step of steps **SD4** to **SD6**, the compression stroke injection is performed in the same manner as above, and then a return is performed.

[0190] Therefore, steps **SC1** and **SC2** of the flow shown in Figure **10** constitute sulfur excessive absorption determining means **40a** for determining that the amount of absorbed SO_x in the catalyst **25** is equal to or more than a predetermined amount. Furthermore, steps **SC8** to **SC11** constitute sulfur detaching means **40b** for detaching SO_x from the NO_x storage material of the catalyst **25**

[0191] More specifically, when the temperature **thg** of the exhaust gas is equal to or more than the preset temperature **thg0**, the sulfur detaching means **40b** controls the air-fuel ratio to be in the vicinity of the theoretical air-fuel ratio so that the oxygen concentration in the exhaust gas is reduced. In addition, the sulfur detaching means **40b** periodically changes the air-fuel ratio alternately between the rich side and the lean side from the theoretical air-fuel. On the other hand, the sulfur detaching means **40b** keeps the temperature of the catalyst **25** high and significantly increases the CO concentration in the exhaust gas by allowing the injector **7** to inject fuel twice, that is, once in the air-intake stroke and once in the compression stroke of the cylinder. In addition, the CO concentration is increased by correcting the fuel injection quantity to be increased.

[0192] Next, the process procedure of EGR control will be described more specifically with reference to the flowchart of Figure **12**. in step **SE1** after the start, various kind of sensor signals such as those from the airflow sensor **12** and the engine revolution number sensor **33** are received, and various kinds of data are input from the memory of the ECU **40**. Then, in step **SE2**, the desired EGR ratio is calculated based on the actual charging efficiency **ce** and the engine revolution number **ne**. An EGR amount that achieves the desired EGR ratio is set as a basic EGR amount **EGRb**. The desired EGR ratio is calculated as follows. The relationship between the charging efficiency ce and the number of engine revolutions ne is previously obtained by bench tests or the like. This relationship is stored in the memory of the ECU **40** as a map.

[0193] Then, in step **SE3**, based on the value of the first flag **F1**, it is determined whether or not the NO_x release control should be performed. When the result of this determination is YES, the procedure goes to step **SE5**. When the result is NO, the procedure goes to step **SE4**. In turn, based on the value of the second flag **F2**, it is determined whether or not the SO_x detachment control should be performed. When the result of this determination is YES, the procedure goes to step **SE5**, where a correction value **EGRc** for correcting the EGR amount either to be increased or decreased is designated as a predetermined value γ (γ <0). When the result is NO, the procedure goes to step **SE6**, where the correction value **EGRc** is made zero (**EGRc** =0). Then, subsequently to steps **SE5** and step **SE6**, in step **SE7**, the basic EGR amount **EGRb** and the correction value **EGRc** are added, so that the final EGR amount **EGRt** is calculated. In step **SE8**, a control signal is output to the EGR valve **27** to drive the EGR valve **27** so that the opening corresponds to the final EGR amount **EGRt**. Then, a return is performed.

[0194] In other words, the opening of the EGR valve **27** is corrected so that the EGR amount is slightly small while the air-fuel ratio in the combustion chamber **4** is kept in the vicinity of the theoretical air-fuel ratio, by performing at least one of the NO_x release control and the SO_x detachment control and by feedback-controlling the fuel injection amount by the injector **7**, as described above.

[0195] Next, the effect of the function of the above embodiment will be described.

[0196] For the engine **1**, for example, as shown in Figure 13, during acceleration, the fuel injection quantity is increased, and the operation is in the $\lambda = 1$ division mode or the enriched mode. In this case, NO_x absorbed in the catalyst **25** is released for reduction and purification. When a steady operation continues, the NO_x absorption excessive state of the catalyst **25** is determined (flag **F1** = 1) based on the travel distance since the last time when NO_x is released and the fuel consumed during that period. At this point, NO_x release control is performed as shown in the flow of Figure **9**.

[0197] On the other hand, for example, when the travel distance of an automobile is as much as several thousands of km, the absorption ability of NO_x may be deteriorated because SO_x is gradually accumulated in the catalyst **25** during operation of the engine **1**. In this case, as shown in the flow of Figure **10**, the sulfur excessive absorption determining means of the engine 1 determines that the amount of absorbed SO_x is excessive, so that the flag **F2** is turned to ON (see Figure **13**). At this point, when the catalyst **25** has a high temperature (for example, 450°C or more), SO_x release control is performed.

[0198] Both the NO_x release and the SO_x release are performed with division of the fuel injection into two operations and feedback control of the air-fuel ratio to be in the vicinity of the air-fuel theoretical ratio. Thus, the oxygen concentration in the exhaust gas is decreased, and the CO concentration and the HC concentration in the exhaust gas are significantly increased and changed periodically. Further, the temperature of the exhaust gas is increased. Therefore, detachment of NO_x and SO_x from the catalyst **25** is facilitated.

[0199] More specifically, the fuel is divided for two operations of injection by the injector **7**, so that a part of the fuel injected in the air-intake stroke of each cylinder **2** is diffused uniformly in the combustion chamber **4** to form a lean air-fuel mixture. On the other hand, the remaining fuel injected in the compression stroke forms an excessively rich air-fuel mixture in the vicinity of the ignition plug **6**. Although this excessively rich air-fuel mixture portion has a high initial combustion speed immediately after ignition, oxygen is insufficient. Therefore, CO is generated readily because of local incomplete combustion. On the other hand, combustion in the surrounding lean air-fuel mixture portion becomes mild, and a part of the fuel is released without being burned completely. As a result, the temperature of the exhaust gas is increased by afterburning and CO is generated more readily. Furthermore, when the number of times of opening of the injector **7** is increased because of division of fuel injection, the ratio of fuel droplets having rough particles that is injected in the early time in the opening is increased, resulting in easy generation of CO.

[0200] Furthermore, the fuel injection quantity by the injector **7** is increased, and the air-fuel ratio in the combustion chamber **4** is controlled to be substantially the theoretical air-fuel ratio, so that the concentrations of the reductant components such as CO and HC in the exhaust gas are increased. At the same time, the fuel injection quantity is feedback-corrected based on signals from the O_2 sensor **24**, so that the air-fuel ratio is periodically changed alternately between the rich side and the lean side. Therefore, the concentrations of CO, HC and the like in the exhaust gas are changed periodically. Thus, the actions of NO_x and SO_x adsorbed onto the catalyst **25** on CO, HC and the like are increased, so that the release of NO_x and SO_x from the catalyst **25** is facilitated.

[0201] As a result, the period of time required for sufficient detachment of SO_x from the catalyst **25**, namely, the period of time during which the air-fuel ratio is controlled to be substantially the theoretical air-fuel ratio only for this purpose can be shortened. Therefore, sufficient regeneration of the catalyst **25** and stable performance for NO_x removal can be achieved with minimal deterioration of the fuel cost.

Absorption of NO_x

[0202] NO_x and HC in the exhaust gas is activated by a precious metal supported by zeolite of the outer catalytic layer **25c**, so that NO is converted to NO_2, and partial oxidation or cracking occurs in HC, which leads to a highly reactive state in terms of energy. For this reason, NO_2 converted from NO by the outer catalytic layer **25c** is more

INSDOCID: <EP 1127603A1 | >

easily absorbed by the NO_x storage material of Ba or other elements, so that its NO_x absorption ratio is increased.

Release of NO_x

[0203] In the catalyst **25**, NO_x is adsorbed onto the surface of the NO_x storage material (e.g., Ba particles) in the form of nitrate. It seems that the nitric acid radical of the nitrate is substituted by supply of CO so that carbonate and nitrogen dioxide are generated. For example, the reaction with Ba particles is as follows.

$$Ba(NO_3)_2 + CO \rightarrow BaCO_3 + NO_2 \uparrow \text{ (coefficients omitted)}$$

Then, nitrogen dioxide is reacted with HC, CO etc. on the catalytic metal for reduction and purification.

$$NO_2 + HC + CO \rightarrow N_2 + H_2O + CO_2 \text{ (coefficients omitted)}$$

[0204] More specifically, since the NO_x is released from the catalyst **25** for reduction and purification, the catalyst can absorb NO_x in the exhaust gas sufficiently again (regeneration of the catalyst).

[0205] In the catalyst **25**, CO and HC in the exhaust gas are adsorbed and retained in zeolite of the outer catalytic layer **25c**, so that the released NO_x can be reduced and purified reliably, as described above. In addition, even if the amount of NO_x released from the catalyst **25** becomes small, CO or HC is not emitted to the air. Therefore, most of the NO_x absorbed in the catalyst **25** can be released. In other words, the catalyst **25** can be regenerated sufficiently.

[0206] Furthermore, since the outer catalytic layer **25c** supports Pt and Rh, NO_2 can be reduced and degraded effectively at a relatively low temperature (e.g., 200 to 250°C). This is especially advantageous when the engine **1** is operated in the stratified combustion state, as in this embodiment. In such stratified combustion, the air-fuel ratio is very lean, and the temperature of the exhaust gas is very low.

Release of SO_x

[0207] Next, regeneration of the catalyst **25** from sulfur poisoning will be described. In the catalyst **25**, SO_x is adsorbed onto the surface of the NO_x storage material (e.g., Ba particles) in the form of sulfate, as in the case of NO_x. It seems that the sulfuric acid radical of the sulfate is substituted by supply of CO so that carbonate and sulfur dioxide are generated. For example, the reaction with Ba particles is as follows.

$$BaSO_4 + CO \rightarrow BaCO_3 + SO_2 \uparrow \text{ (coefficients omitted)}$$

[0208] Furthermore, when the CO concentration becomes high, a so-called water gas shift reaction proceeds between CO and water H_2O in the exhaust gas, thereby generating hydrogen in the reaction site of the catalyst.

$$CO + H_2O \rightarrow H_2 + CO_2$$

Then, the action of hydrogen causes SO_x to be detached in the form of hydrogen sulfide. This also facilitates the detachment of the sulfur component from the catalyst **25**. Since the water gas shift reaction proceeds even in a relatively low temperature, the detachment of SO_x can be facilitated without significantly raising the temperature of the catalyst **25**.

[0209] Furthermore, zeolite is supported by the outer catalytic layer **25c** of the catalyst **25**, and zeolite causes partial oxidation of HC in the exhaust gas so that HC is converted to HCO or CO. Therefore, the CO concentration that affects SO_x adsorbed onto the surface of the NO_x storage material of the inner catalytic layer **25b** is further increased.

[0210] Furthermore, when elements (K, Sr, Mg or La) other than Ba are more susceptible to sulfur poisoning than Ba, this makes the sulfur poisoning of Ba relatively small, so that the deterioration of NO_x absorption ability after sulfur poisoning becomes small. When the other elements (K, Sr, Mg or La) can be regenerated more easily from sulfur poisoning than Ba, the NO_x absorption ability after regeneration becomes high. Furthermore, when the presence of the other elements (K, Sr, Mg or La) leads to an increase of the specific surface area of the NO_x storage material or the reaction site, the NO_x absorption ability of the NO_x storage material becomes high. Furthermore, when the other elements serve to prevent sintering by heat of Ba, heat deterioration due to the sulfur detachment treatment of the NO_x storage material can be prevented.

EPODOC <EP 1127603A1>

[0211] Alumina and a ceria-zirconia mixed oxide constitute the support, and alumina is useful to ensure the heat resistance of the catalyst, and the mixed oxide facilitates a purification reaction of three substances of HC, CO and NO_x when the engine is operated in the vicinity of $\lambda = 1$, and is advantageous for improvement of the sulfur poisoning resistance of the catalyst.

Specific examples of the catalyst

Constitution of the catalyst

[0212] Figure **14** shows the catalyst **25** for purifying the exhaust gas. The catalyst **25** is a laminate comprising a monolith carrier **25a**, an inner catalytic layer **25b**, and an outer catalytic layer **25c**. The monolith carrier **25a** is made of for example, cordierite, which is a carrier material having an excellent heat resistance. The inner catalytic layer **25b** is formed near the surface of the carrier **25a**, and the outer catalytic layer **25c** is formed away from the surface of the carrier **25a**.

[0213] The inner catalytic layer **25b** includes a first precious metal component (e.g., Pt), Ba, K, Sr and Mg as NO_x storage materials, a first support supporting the first precious metal and the NO_x storage materials, and a binder for binding the support powder for retention in the carrier. In this case, the first support is formed of a mixture of alumina and a $CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide.

[0214] The outer catalytic layer **25c** includes a second precious metal component (e.g., Pt, Rh), Ba, K, Sr and Mg as NO_x storage materials, a second support supporting the precious metal and the NO_x storage materials, and a binder for binding the second support powder for retention in the carrier. In this case, the second support is formed of zeolite.

[0215] The content of impurities in each of the catalytic layers **25b** and **25c** is 1% or less.

(Production method of the catalyst **25**)

[0216] The basic method for producing the catalyst **25** is as follows.

[0217] First, the first support (a mixture of alumina and a $CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide), the binder, and water are mixed to form slurry. The monolith carrier is wash-coated with this slurry and dried and calcined, so that an inner coating layer is formed.

[0218] Then, the second precious metal is supported by the second support (zeolite) by evaporation to dryness so that catalyst power is formed. Then, the catalyst power, the binder and water are mixed to form slurry. The monolith carrier provided with the inner coating layer is wash-coatedwith this slurry and dried and calcined, so that an outer coating layer is formed on the inner coating layer.

[0219] Then, a solution of the first precious metal component, and solutions of Ba component, K component, Sr component and Mg component are mixed to prepare a mixed solution. Then, the inner coating layer and the outer coating layer are impregnated with the mixed solution at the same time, and are dried and calcined.

[0220] In this manner, the inner catalytic layer and the outer catalytic layer are formed as the inner coating layer and the outer coating layer, respectively.

(Use form of the catalyst **25**)

[0221] As shown in Figure **15**, for example, the catalyst **25** is provided in the emission passage **22** for emitting an exhaust gas from the lean combustion engine **4** for automobiles. The provision site corresponds to a site immediate downstream of an emission manifold. The catalyst **25** stores NO_x contained in the exhaust gas in Ba, K, Sr and Mg during lean combustion operation. Then, during operation of combustion at the theoretical air-fuel ratio or rich combustion operation ($\lambda \leq 1$), in the catalyst **25**, NO_x released from Ba or the like is reacted with HC, CO and H_2 to purify the exhaust gas as well as the ternary catalyst. More specifically, the catalyst **25** has a lean NO_x purification function, and the concentration of oxygen in the exhaust gas during lean combustion operation is for example, 4 or 5% to 20%, and the air-fuel ratio A/F is 18 to 150. On the other hand, the concentration of oxygen during rich combustion operation is 0.5% or less.

[0222] Furthermore, although the catalyst **25** has a lean NO_x purification function, when the lean combustion operation continues for a long time, the amount of stored NO_x of the catalyst **25** is saturated so that the NO_x purification performance is deteriorated. Therefore, control is performed so that a cycle as follows is repeated. A lean combustion operation is performed for 2 to 3 minutes, during which NO_x is stored in the NO_x storage material. Then, a rich combustion operation is performed for 1 to 5 seconds, during which the stored NO_x is released for purification.

[0223] Furthermore, when it is determined that the amount of the sulfur component absorbed in the NO_x storage materials (Ba, K, Sr and Mg) contained in the inner catalytic layer **25b** and the outer catalytic layer **25c** is excessive, the air-fuel ratio in the combustion chamber is made rich, and ignition retard control for delaying an ignition time is

INSDOCID: <EP 1127603A1 I >

performed for 2 to 10 minutes. Thus, the temperature of the exhaust gas is raised, so that the temperature of the NO_x storage materials is also increased. Thus, the sulfur component is detached from the sulfur-poisoned NO_x storage materials for regeneration.

[0224] Since the precious metals as catalytic metals are supported in the inner catalytic layer **25b** and the outer catalytic layer **25c**, NO_x and HC in the exhaust gas are activated on the surface of the precious metals, and oxygen activated from the mixed oxide is supplied. Therefore, an oxidation reaction of NO in the exhaust gas to NO_2 and a partial oxidation reaction of HC proceed smoothly. Since NO_2 and the partially oxidized HC are highly reactive in terms of energy, reduction of NO_x and oxidation of HC in the catalyst **25** proceed efficiently.

[0225] More specifically, at a lean air-fuel ratio, in the outer catalytic layer **25c**, HC that has been stored in zeolite when the catalyst has a low temperature is released with increasing the temperature of the catalyst, and HC is reacted with NO in the exhaust gas without being partially oxidized, or HC is reacted with NO after being partially oxidized and thus NO_x is purified. In the inner catalytic layer **25b**, NO_2 generated by oxidation of NO in the outer catalytic layer **25c** is stored in the NO_x storage materials, and apparently NO_x is purified. NO_2 stored in the NO_x storage materials is reacted with partially oxidized HC that has been activated on the precious metals of the inner catalytic layer **25b** and the outer catalytic layer **25c** when the air-fuel ratio is turned to be rich so that NO_2 is degraded and purified. Therefore, the outer catalytic layer **25c** exerts a function as a catalyst for selective reduction NO_x purification, and the inner catalytic layer **25b** exerts a function as a catalyst for lean NO_x purification.

[0226] In the above embodiment, the catalyst **25** is a lean NO_x catalyst, but is not limited thereto and can be a ternary catalyst comprising a Ce-Zr-Sr mixed oxide as an oxygen storage material. In this case, even if the catalyst has been exposed to a high temperature atmosphere for a long time, the mixed oxide can act effectively as an oxygen supply source for HC oxidation, so that HC can be oxidized and eliminated. As a result, a high HC purification performance can be obtained.

[0227] Furthermore, in the above embodiment, the catalyst **25** is used to purify an exhaust gas of a gasoline engine, but is not limited thereto and can be used to purify an exhaust gas of a diesel engine having an air-fuel ratio A/F of 18 to 50. In this case, for regeneration of the NO_x storage material of the catalyst **25**, injection retard control for delaying the fuel injection time is performed to raise the temperature of the exhaust gas.

Experiment 1

[0228] Tests were conducted to evaluate the heat resistance and the sulfur poisoning resistance of catalysts of examples as shown below.

<Preparation of catalysts for evaluation>

-Example **1**-

[0229] A catalyst of Example **1** was prepared in the following manner. Formation of an inner coating layer

[0230] γ-alumina, $CeO_2 \cdot ZrO_2 \cdot Sm_2O_3$ as a mixed oxide (a mass composition ratio of CeO_2:ZrO_2:Sm_2O_3 of 23:73:4)and an alumina binder were weighed and mixed so that the support amount of γ-alumina was 150g/L and the support amount of the mixed oxide was 150g/L, and the support amount of the alumina binder was 30g/L. Herein, the support amount refers to an amount of dry mass per L of a carrier when the substance is supported in the honeycomb carrier that is described later. Then, ion exchanged water was added thereto to prepare slurry. A monolith carrier made of cordierite was immersed in this slurry and lifted up, and excess slurry was blown off. In this manner, the carrier was wash-coated with the slurry. Then, this was dried at a temperature of 150°C for one hour, and calcined at a temperature of 540°C for two hours to form an inner coating layer. The conditions of drying and calcining are the same as those described below.

Formation of an outer coating layer

[0231] An aqueous solutions of dinitrodiamine platinum and an aqueous solution of rhodium nitrate were weighed and mixed so that the Pt support amount was 0.5g/L and the Rh support amount was 0.006g/L, and the mixture was combined with MFI type zeolite (SiO_2/Al_2O_3 = 80) and was subjected to spray to dryness by spray-drying and further dried and calcined to prepare catalyst powder. The amount of the combination of Pt and Rh in the catalyst power was about 2.5 mass percent.

[0232] Then, the Pt-Rh/MFI catalyst powder and the alumina binder were weighed and mixed so that the support amount of the catalyst power was 20g/L and the support amount of the binder was 4g/L, and an ion exchanged water was added to the mixture, so that a slurry was prepared. The carrier provided with the inner coating layer was wash-coated with the slurry, and then dried and calcined to form an outer coating layer.

Impregnation process

[0233] An aqueous solution of dinitrodiamine platinum nitrate, an aqueous solution of barium acetate, an aqueous solutionof potassium acetate, an aqueous solution of strontium acetate, and an aqueous solution of magnesium acetate were weighed and mixed so that the Pt support amount was 3g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Sr support amount was 10g/L, and the Mg support amount was 10g/L to prepare a mixed solution.

[0234] Then, the inner coating layer and the outer coating layer of the carrier were impregnated with the mixed solution, and were dried and calcined.

[0235] The content of impurities in the obtained catalyst was less than 1%. This also applies to other examples of catalysts described below.

-Example **2**-

[0236] A catalyst of Example **2** was prepared by the same method and under the same conditions as in Example **1** except that $CeO_2 \cdot ZrO_2 \cdot La_2O_3$ (a mass composition ratio of CeO_2:ZrO_2:La_2O_3 of 23:73:4) was used as a mixed oxide for the inner coating layer.

-Example **3**-

[0237] A catalyst of Example **3** was prepared by the same method and under the same conditions as in Example **1** except that $CeO_2 \cdot ZrO_2 \cdot In_2O_3$ (a mass composition ratio of CeO_2:ZrO_2:In_2O_3 of 23:73:4) was used as a mixed oxide for the inner coating layer.

-Example **4**-

[0238] A catalyst of Example **4** was prepared by the same method and under the same conditions as in Example **1** except that $CeO_2 \cdot ZrO_2 \cdot SrO$ (a mass composition ratio of CeO_2:ZrO_2:SrO of 23:73:4) was used as a mixed oxide for the inner coating layer.

-Reference example-

[0239] A catalyst for reference was prepared by the same method and under the same conditions as in Example **1** except that CeO_2 ZrO_2 (a mass composition ratio of CeO_2:ZrO_2 of 75:25) was used as a mixed oxide for the inner coating layer.

[0240] For reference, the specific surface area and the oxygen storage ability after aging at 1000°C of the mixed oxide of each catalyst were measured. Table **1** shows the results.

Table 1

		Ex. 1	Ex.2	Ex.3	Ex.4	Reference Ex.
Specific surface area	m^2/g	30	40	4	38	25
Oxygen storage ability	μmol/g	150	150	200	140	130

<Evaluation **1**:Heat resistance>

Evaluation test method

[0241] The catalysts of Examples **1** to **4** and Reference Example were heated in an ambient atmosphere at 900°C for 24 hours.

[0242] Then, NO_x purification ratios were measured according to the methods described below.

-Method for measuring the NO_x purification ratio-

[0243] The catalyst was attached to a fixed floor flow-through reaction evaluation apparatus, and as shown in Figure **16**, a simulated exhaust gas (gas composition **A**) at a lean air-fuel ratio was allowed to flow for 60 seconds, and then the gas composition was switched and a simulated exhaust gas having a rich air-fuel ratio (gas composition **B**) was allowed to flow for 60 seconds. These operations constitute one cycle, and this cycle was repeated 5 times. Then, the

INSDOCID: <EP 1127603A1 I >

gas composition was switched to that at the lean air-fuel ratio (gas composition **A**), and for 60 seconds and 130 seconds from this point of switching (600 seconds later from the test start), the NO_x purification ratio (lean NO_x purification ratio) was measured. The temperature of the catalyst and the temperature of the simulated exhaust gas were 350°C. The gas composition was shown in Table **2**. The space velocity **SV** was 25000h^{-1}.

Table 2

	Gas composition A	Gas composition B
	Lean	Rich
$HC(C_3H_6)$	4000ppm	4000ppm
NO	260ppm	260ppm
CO	0.16%	0.16%
CO_2	9.75%	9.75%
H_2	650ppm	650ppm
O_2	7%	0.5%
N_2	the remaining	the remaining

(Test Results)

[0244] Figures **17** and **18** show the NO_x purification ratios for 60 seconds and 130 seconds after the switching point.

[0245] As shown in Figures **17** and **18**, in both cases of 60 and 130 seconds, Example **4** where a $CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide was used has a higher NO_x purification ratio than those of Examples **1** to **3**, and thus has excellent heat resistance. According to Table **1**, although Examples **2** and **4** have substantially equal specific surface areas and oxygen storage abilities, Example **4** exhibited a better NO_x purification ratio. This may be because Sr highly activates oxygen that comes in and out the mixed oxide so that the activity thereof is not lost even after the mixed oxide is exposed to a high temperature atmosphere for a long time. Furthermore, according to Table **1**, although the mixed oxide of Example **3** has large oxygen storage ability, the NO_x purification ratio thereof was small. This seems to be because the active area as an oxygen storage material was small.

[0246] Example **4** has a slightly poorer NO_x purification ratio than that of Reference Example. However, in Reference Example, $CeO_2 : ZrO_2 = 75:25$, whereas in Example **4**, $CeO_2 : ZrO_2 : SrO = 23:73:4$. Therefore, they cannot be compared directly. However, the following is noteworthy. It is Ce that has the oxygen storage and release abilities; and Example **4** has a small amount of the Ce component. Therefore, it is predicted that the NO_x purification ratio thereof will be low. In reality, however, Example **4** has a comparable NO_x purification ratio to Reference Example.

<Evaluation **2**: Sulfur poisoning resistance and regeneration properties>

(Evaluation test method)

[0247] For each catalyst of Examples **1** to **4** and Reference Example, a fresh catalyst that has not been subjected to a deterioration treatment, and a catalyst that has been subjected to a SO_2 treatment (sulfur poisoning deterioration treatment) that is described below were prepared. For Example **4** and Reference Example, a catalyst that has been subjected to a regeneration treatment that is described below after the SO_2 treatment was prepared as well.

[0248] Then, the NO_x purification ratio was measured by the same method and under the same conditions as in Evaluation **1**.

-SO_2 treatment-

[0249] A SO_2 treatment was performed in the following manner. A simulated exhaust gas constituted by 50ppm of SO_2 and 20% of O_2 and N_2 was passed through the catalyst attached to a fixed floor flow-through reaction evaluation apparatus for 60 minutes. The temperature of the catalyst at the inlet was 350°C. The space velocity **SV** was 55000h^{-1}.

-Regeneration treatment-

[0250] A regeneration treatment was performed in the following manner. A simulated exhaust gas having a gas composition A/F = 14.7 ±0.9 was passed through the catalyst attached to a fixed floor flow-through reaction evaluation

SDOCID: <EP 1127603A1 >

apparatus for 10 minutes. The temperature of the catalyst at the inlet was 600°C. The space velocity **SV** was 120000h^{-1}.

(Test Results)

[0251] Figures **19** and **20** show the NO_x purification ratios for 60 seconds and 130 seconds after the switching point.
[0252] As shown in Figures **19** and **20**, in both cases of 60 and 130 seconds, Examples **1** to **4** have higher NO_x purification ratios than that of Reference Example, and thus have more excellent sulfur poisoning resistance. The reason for this is not clear, but it seems that the presence of Sm, La, In or Sr provides fine NO_x storage materials so that the surface areas thereof were large, and therefore the catalysts were less susceptible to sulfur poisoning. Consequently, sulfur poisoning deterioration of the NO_x storage materials can be suppressed by contacting the exhaust gas containing the sulfur component with the lean NO_x purifying catalyst containing Sm, La, In or Sr.
[0253] Furthermore, regeneration of the NO_x purification performance can be confirmed in Example **4** and Reference Example to which the regeneration treatment was performed. Especially, Example **4** exhibits a very high regeneration performance. Therefore, it is preferable to raise the temperature of the catalyst when it is determined that the lean NO_x purifying catalyst containing Sm, La, In or Sr was sulfur-poisoned. This seems to realize high regeneration ability from sulfur poisoning of the catalyst.

Experiment **2**

[0254] Tests for evaluation were conducted regarding the heat resistance and the sulfur poisoning resistance of the catalysts of the following examples.

<Preparation of catalysts for evaluation>

-Example **5**-

[0255] A catalyst of Example **5** was prepared in the following manner. Formation of an inner coating layer
[0256] γ-alumina, a Ce-Zr-Sr mixed oxide (a $CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide, a mass composition ratio of CeO_2:ZrO_2:SrO of 73.3:25.7:1) and an alumina binder were weighed and mixed so that the support amount of γ-alumina was 160g/L, the support amount of the Ce-Zr-Sr mixed oxide was 160g/L, and the support amount of the binder was 30g/L. Then, ion exchanged water was added thereto to prepare slurry.
[0257] A honeycomb carrier was wash-coated with a half amount of the slurry, and dried and calcined to form an inner coating layer. Then, the inner coating layer was wash-coated with the other half of the amount of the slurry, and dried and calcined in the same manner to form an outer coating layer.

Impregnation process

[0258] Aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, strontium acetate, and magnesium acetate were weighed and mixed so that the Pt support amount was 3.5g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Sr support amount was 10g/L, and the Mg support amount was 10g/L to prepare a mixed solution. Then, the inner coating layer and the outer coating layer of the carrier were impregnated with the mixed solution, and were dried and calcined.

-Example **6**-

[0259] A catalyst of Example **6** was prepared by the same method and under the same conditions as in Example 5 except that a Ce-Zr mixed oxide (a $CeO_2 \cdot ZrO_2$ mixed oxide, a mass composition ratio of CeO_2:ZrO_2 of 74:26) was used as a mixed oxide.

<Evaluation **1**:Heat resistance>

[0260] The catalysts of Examples **5** and **6** were heated in an ambient atmosphere at 900°C for 24 hours. Thereafter, NO_x purification ratios (lean NO_x purification ratios) were measured for 60 seconds and 130 seconds from the point at which the gas composition was switched to a lean air-fuel ratio (gas composition A). Figure **21** shows the NO_x purification ratios measured for 60 seconds from the point of switching to a lean air-fuel ratio, and Figure **22** shows the NO_x purification ratios measured for 130 seconds from the point of switching to a lean air-fuel ratio.
[0261] Figures **21** and **22** show that Example **5** where the mixed oxide contains Sr has a higher NO_x purification ratio than that of Example **6** that contains no Sr, although Example **5** has a slightly smaller amount of CeO_2 than that of

NSDOCID: <EP_____1127603A1_I_>

Example **6**. This indicates that using a Ce-Zr-Sr double compound has an effect on improving the heat resistance of the catalyst.

<Evaluation **2:** Sulfur poisoning resistance and regeneration properties>

[0262] For each of Examples **5** and **6**, a fresh catalyst that has not been subjected to a deterioration treatment, a catalyst that has been subjected to a SO_2 treatment (sulfur poisoning deterioration treatment) and a catalyst that has been subjected to a regeneration treatment after the SO_2 treatment were prepared. Then, the NO_x purification ratio was measured by the same method and under the same conditions as in Evaluation **1**. The SO_2 treatment and the regeneration treatment were the same as those in Experiment **1**. Figures **23** and **24** show the results.

[0263] According to Figures **23** and **24**, Example **5** where the mixed oxide contains Sr has substantially no difference from Example **6** that contains no Sr in the fresh catalyst. However, Example **5** has higher NO_x purification ratios after the SO_2 treatment and the regeneration treatment. These results indicate that using a Ce-Zr-Sr mixed oxide has an effect on the sulfur poisoning resistance and the regeneration properties of the catalyst.

Experiment **3**

[0264] A catalyst of Example **7** was prepared and the NO_x purification ratio for 60 seconds after switching to a lean air-fuel ratio was measured by the test of Evaluation **1** and was compared with the test results of Examples **5** and **6**. Thus, the effect of the ratio of SrO in the mixed oxide on the NO_x purification ratio was investigated.

-Example **7**-

[0265] A catalyst of Example **7** was prepared by the same method and under the same conditions as in Example **5** except that a Ce-Zr-Sr mixed oxide (a $CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide, a mass composition ratio of CeO_2:ZrO_2 :SrO of 71:25:4) was used as a mixed oxide.

[0266] Figure **25** shows the results. According to Figure **25**, Example **7** that has a larger SrO ratio in the mixed oxide has a slightly lower NO_x purification ratio for 60 seconds after switching to a lean ratio than that of Example **6** that contains no Sr in the mixed oxide. Therefore, the results indicate that the smaller ratios of SrO in the mixed oxide are better. Preferable ratios are 0.5 to 2.0 mass percent.

<NO_x storage materials>

[0267] Catalysts of Examples **1'** to **11'** were prepared in the following manner, and the effects of the type of the NO_x storage materials on the NO_x purification ratio, the sulfur poisoning resistance and the regeneration properties from sulfur poisoning were investigated.

Example **1'**

Formation of Pt-Rh/MFI catalyst powder

[0268] Aqueous solutions of dinitrodiamine platinum and rhodium nitrate were weighed and mixed so that the Pt support amount was 0.5g/L and the Rh support amount was 0.006g/L. Herein, the support amount refers to an amount of dry mass per L of a carrier when the substance is supported in the honeycomb carrier, and the same applies to the following examples. The mixture was combined with MFI type zeolite (SiO_2/Al_2O_3 = 80) and was subjected to spray to dryness by spray-drying and further dried and calcined to prepare catalyst powder. The amount of the combination of Pt and Rh in the catalyst power was about 2.5 wt%.

Preparation of a mixed solution (for impregnation)

[0269] Aqueous solutions of dinitrodiamine platinum nitrate and barium acetate were weighed and mixed so that the Pt support amount was 6.0g/L and the Ba support amount was 30g/L to prepare a mixed solution.

Formation of an inner coating layer

[0270] γ-alumina, a $CeO_2 \cdot ZrO_2$ mixed oxide and an alumina binder were weighed and mixed so that the support amount of γ-alumina was 150g/L, the support amount of the mixed oxide was 150g/L, and the support amount of the binder was 30g/L. Then, ion exchanged water was added thereto to prepare slurry. A honeycomb carrier (a volume of

25mL, a mass per L of the carrier of 420g/L) made of cordierite was immersed in this slurry and lifted up, and excess slurry was blown off. In this manner, the carrier was wash-coated with the slurry. Then, this was dried and calcined to form an inner coating layer.

Formation of an outer coating layer

[0271] The Pt-Rh/MFI catalyst powder and the alumina binder were weighed and mixed so that the support amount of the catalyst power was 20g/L, and the support amount of the binder was 4g/L, and an ion exchanged water was added thereto to prepare a slurry. The carrier provided with the inner coating layer was wash-coated with the slurry, and then dried and calcined to form an outer coating layer.

Impregnation process

[0272] The inner coating layer and the outer coating layer of the carrier were impregnated with the mixed solution, and were dried and calcined.

[0273] In this catalyst, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

[0274] The content of impurities in the obtained catalyst was less than 1%. This also applies to other examples of catalysts described below.

Example **2'**

[0275] The catalyst was prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate and barium acetate were weighed and mixed so that the Pt support amount was 6.0g/L and the Ba support amount was 50g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example **3'**

[0276] The catalyst was prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, strontium acetate, and lanthanum acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the Sr support amount was 10g/L, and the La support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example **4'**

[0277] The catalyst was prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, magnesium acetate, and lanthanum acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the Mg support amount was 10g/L, and the La support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example **5'**

[0278] The catalyst was prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, potassium acetate, and strontium acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the K support amount was 10g/L, and the Sr support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example **6'**

[0279] The catalyst was prepared by the same method and under the same conditions as in Example **1'**, except that

NSDOCID: <EP 1127603A1 I >

aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, strontium acetate, and magnesium acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the Sr support amount was 10g/L, and the Mg support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example 7'

[0280] The catalyst was prepared by the same method and under the same conditions as in Example 1', except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, and potassium acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, and the K support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example 8'

[0281] The catalyst was prepared by the same method and under the same conditions as in Example 1', except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, potassium acetate and magnesium acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the K support amount was 10g/L, and the Mg support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example 9'

[0282] The catalyst was prepared by the same method and under the same conditions as in Example 1', except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, potassium acetate, and lanthanum acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the K support amount was 10g/L, and the La support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example 10'

[0283] The catalyst was prepared by the same method and under the same conditions as in Example 1', except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, potassium acetate, strontium acetate, magnesium acetate, and lanthanum acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L, the K support amount was 10g/L, the Sr support amount was 10g/L, the Mg support amount was 10g/L, and the La support amount was 10g/L to prepare a mixed solution. In this example as well, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.0g/L by the mixed solution. Therefore, the total Pt support amount is 6.5g/L.

Example 11'

[0284] The catalyst was prepared by the same method and under the same conditions as in Example 1', except that aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, strontium acetate, and magnesium acetate were weighed and mixed so that the Pt support amount was 6.5g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Sr support amount was 10g/L, and the Mg support amount was 10g/L to prepare a mixed solution.

[0285] In this example, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 6.5g/L by the mixed solution. Therefore, the total Pt support amount is 7.0g/L. Regarding Rh, Rh is supported in an amount of 0.006g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 0.1g/L by the mixed solution. Therefore, the total Rh support amount is 0.106g/L.

Evaluation test of the catalysts

Method for measuring the NO_x purification ratio

[0286] A method for measuring the NO_x purification ratio is as follows. Each catalyst was attached to a fixed floor flow-through reaction evaluation apparatus, and a simulated exhaust gas having a lean air-fuel ratio shown as gas composition **A** in Table **3** was passed through the catalyst until the NO_x purification ratio became stable. Then, the simulated exhaust gas with its gas composition switched to one having a rich air-fuel ratio shown as gas composition **B** in Table **3** was passed through the catalyst for 3 minutes. Thus, NO_x that were previously absorbed in the NO_x storage materials were detached. Thereafter, the simulated exhaust gas was switched to the one having the gas composition **A**, and for 130 seconds from this point of switching, the NO_x purification ratio (lean NO_x purification ratio) was measured.

[0287] The temperature for measurement of the NO_x purification ratio (the temperature of the gas at the inlet of the catalyst) was 350°C or 450°C. The space velocity **SV** was 55000h^{-1} except in Example **11'**. The space velocity **SV** in Example **11'** was 25000h^{-1}. The NO_x purification ratio was measured with a fresh catalyst that has not been subjected to a deterioration treatment, a catalyst that has been subjected to a SO_2 treatment (sulfur poisoning deterioration treatment), a catalyst that has been subjected to a regeneration treatment after the SO_2 treatment, and a catalyst that has been subjected to a heat deterioration treatment. The SO_2 treatment, the regeneration treatment, the heat deterioration treatment were performed under the following conditions.

SO_2 treatment

[0288] The SO_2 treatment was performed by passing a simulated exhaust gas having a gas composition C shown in Table 3 through the catalyst attached to a fixed floor flow-through reaction evaluation apparatus for 60 minutes. The temperature of the gas at the inlet of the catalyst was 350°C. The space velocity **SV** was 55000h^{-1}.

Regeneration treatment

[0289] The regeneration treatment was performed by switching three kinds of simulated exhaust gases shown in Table **4** as appropriate and passing the simulated exhaust gases through the catalyst attached to a fixed floor flow-through reaction evaluation apparatus for 10 minutes. In this case, switching of the simulated gases was performed so that the gas composition was changed in the order of 1. A/F = 14.7→ 2. A/F = 13.8→ 3. A/F = 14.7 → 4. A/F = 15.6 (→ 1 A/F = 14.7) with a cycle of 1 second. The temperature of the gas at the inlet of the catalyst was 600°C. The space velocity **SV** was 120000h^{-1}.

Heat deterioration treatment

[0290] The heat deterioration treatment was to allow the catalyst to be heated at 900°C in an ambient atmosphere for 24 hours.

Table 3

	Gas composition A	Gas composition B	Gas composition C
	Lean	Rich	SO_2 treatment
$HC(C_3H_6)$	4000ppm	4000ppm	-
NO	250ppm	250ppm	-
CO	0.15%	0.15%	-
CO_2	10%	10%	-
H_2	650ppm	650ppm	-
O_2	7%	0.5%	20%
H_2O	10%	10%	-
SO_2	-	-	50ppm
N_2	the remaining	the remaining	the remaining

NSDOCID: <EP 1127603A1 | >

Table 4

Regeneration treatment			
Component	A/F = 14.7	A/F = 13.8	A/F = 15.6
$HC(C_3H_6)$	560ppm	560ppm	560ppm
NO	1000ppm	1000ppm	1000ppm
CO	0.60%	2.60%	0.60%
CO_2	13.90%	13.90%	13.90%
H_2	0.20%	0.90%	0.20%
O_2	0.600%	0.600%	1.9%
H_2O	10%	10%	10%
SO_2	-	-	-
N_2	the remaining	the remaining	the remaining

[0291] Figure **26** shows the results of the measurement of the NO_x purification ratios when the catalysts are fresh, after the SO_2 treatment, and after the regeneration treatment after the SO_2 treatment (where the gas temperature at the inlet of the catalyst was 350°C in all the cases). According to Figure **26**, there is no significant difference in the NO_x purification ratio between the catalysts when they are fresh. However, regarding the NO_x purification ratio after the SO_2 treatment, Examples **3'** to **11'** where other elements (at least one of K, Sr, Mg and La) were used together with Ba have higher ratios than those of Examples **1'** and **2'** where the NO_x storage material is constituted only by Ba. In particular, this tendency is significant in the examples that contain K. On the other hand, regarding the NO_x purification ratio after the regeneration treatment, the examples that contain K tend to have high ratios except Example **5'**, and this tendency is significant in the examples that contain Mg or La in addition to K.

[0292] Figure **27** shows the NO_x purification ratios when the catalyst is fresh and after the heat treatment (heat deterioration treatment) when the gas temperature at the inlet of the catalyst was 350°C. According to Figure **27**, although there are no significant effects on the sulfur poisoning resistance (NO_x purification characteristics after the regeneration treatment), Examples **3'** to **6'** tend to have higher NO_x purification ratios after the heat treatment. In particular, this tendency is significant in Example **5'**. This tendency applies to the NO_x purifications when the catalyst is fresh and after heat treatment (heat deterioration treatment) when the gas temperature at the inlet of the catalyst was 450°C, which is shown in Figure **28**. Thus, although there are no significant effects on the sulfur poisoning resistance in Examples **3'** to **6'**, excellent effects on the heat resistance were exhibited. It can be said that Examples **3'** to **6'** are advantageous for maintaining the NO_x absorption ability by the regeneration treatment, in view of the fact that the regeneration treatment is performed at a relatively high temperature.

[0293] Furthermore, according to Figure **28**, Examples **5'**, **8'** and **9'**, which contain K in addition to Ba, and further contain at least one of Sr, Mg and La, have high NO_x purification ratios at 450°C when they are fresh. This means that it is possible to drive at a lean air-fuel ratio without significantly emitting NO_x, even if the temperature of the exhaust gas is high, such as high-speed driving.

[Ba-K-Sr based NO_x storage materials]

[0294] Catalysts were prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, and strontium acetate were weighed and mixed so that the Pt support amount was 3.0g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Sr support amount was 0g/L, 5g/L, 10g/L, 15g/L, 20g/L and 30g/L to prepare mixed solutions.

[0295] In this example, Pt is supported in an amount of 0.5g/L by the Pt-Rh/MFI catalyst powder of the outer coating layer and in an amount of 3.0g/L by the mixed solution. Therefore, the total Pt support amount is 3.5g/L. Rh is supported in an amount of 0.006g/L by the Pt-Rh/MFI catalyst powder and in an amount of 0.1g/L by the mixed solution. Therefore, the total Rh support amount is 0.106g/L.

[0296] For comparison, a comparative catalyst was prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, and barium acetate were weighed and mixed so that the Pt support amount was 3.0g/L, the Rh support amount was 0.1g/L, and the Ba support amount was 30g/L (the K support amount was 0, the Sr support amount was 0) to prepare mixed solutions. In

this comparative catalyst as well, the total Pt support amount is 3.5g/L, and the total Rh support amount is 0.106g/L.

[0297] The NO_x purification ratios of the catalysts having varied Sr support amounts and the comparative catalyst were measured in the same manner as in the previously described evaluation test when they were fresh, after the SO_2 treatment and after the regeneration treatment. Figure **29** shows the results of the catalysts with varied Sr support amounts. According to Figure **29**, when Sr is supported, the NO_x purification ratios after the regeneration treatment are higher than those in no Sr support amount. However, when the support amount is 20g/L or more, the NO_x purification ratios after the regeneration treatment are deteriorated. A preferable Sr support amount is at least 5g/L and less than 20g/L, or at least 10g/L and less than 20g/L, most preferably, 15g/L. Therefore, the range from 13g/L to 17g/L is advantageous for keeping the NO_x purification ratio after regeneration treatment high.

[0298] Furthermore, for the comparative catalyst, the NO_x purification ratio when the catalyst is fresh is 72%, the NO_x purification ratio after the SO_2 treatment is 41%, and the NO_x purification ratio after the regeneration treatment is 63%. Therefore, when K and Sr, in addition to Ba, are supported, until the Sr support amount reaches 20g/L, all the NO_x purification ratios when the catalyst is fresh, after the SO_2 treatment and after the regeneration treatment are higher than those of the comparative catalyst, which contains only Ba.

[0299] Figure **30** shows the results of measurement of the NO_x purification ratios of the catalysts having varied Sr support amounts and the comparative catalyst after the heat deterioration treatment as previously described. The dotted broken line in Figure **30** indicates the NO_x purification ratio of the comparative catalyst. The space velocity was 25000h^{-1}. According to Figure **30**, when the Sr support amount is 30g/L or more, the heat resistance of the catalyst becomes lower than that of the comparative catalyst. However, the heat resistance is improved at a support amount of less that 30g/L. This is advantageous for regeneration.

[Ba-K-Mg based NO_x storage materials]

[0300] The catalysts were prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, and magnesium acetate were weighed and mixed so that the Pt support amount was 3.0g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Mg support amount was 0g/L, 5g/L, 10g/L, 15g/L, and 20g/L to prepare mixed solutions. In this example as well, the total Pt support amount is 3.5g/L, and the total Rh support amount is 0.106g/L.

[0301] The NO_x purification ratios of the catalysts having varied Mg support amounts were measured in the same manner as in the previously described evaluation test when they were fresh, after the SO_2 treatment and after the regeneration treatment. Figure **31** shows the results thereof. According to Figure **31**, when Mg is supported, the NO_x purification ratios after the regeneration treatment are higher than those in no Mg support amount. When the support amount is 10g/L, the NO_x purification ratio after the regeneration treatment is highest. Support amounts of Mg of 3g/L to 17g/L, or 5g/L to 15g/L are advantageous for keeping the NO_x purification ratio after regeneration treatment high.

[0302] Furthermore, for the comparative catalyst (which has been described in the above item of Ba-K-Sr based NO_x storage material), the NO_x purification ratio when the catalyst is fresh is 72%, the NO_x purification ratio after the SO_2 treatment is 41%, and the NO_x purification ratio after the regeneration treatment is 63%. Therefore, when K and Mg, in addition to Ba, are supported, all the NO_x purification ratios when the catalyst is fresh, after the SO_2 treatment and after the regeneration treatment are higher than those of the comparative catalyst, which contains only Ba.

[0303] Figure **32** shows the results of measurement of the NO_x purification ratios of the catalysts having varied Mg support amounts and the comparative catalyst after the heat deterioration treatment as previously described. The dotted broken line in Figure **32** indicates the NO_x purification ratio of the comparative catalyst. The space velocity was 25000h^{-1}. According to Figure **32**, up to a Mg support amount of 20g/L, the heat resistance of the catalyst is improved. This is advantageous for regeneration.

[Ba-K-Sr-Mg based NO_x storage materials]

[0304] Catalysts were prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, strontium acetate and magnesium acetate were weighed and mixed so that the Pt support amount was 3.0g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Mg support amount was 5g/L and the Sr support amount was varied to prepare mixed solutions. Furthermore, catalysts were prepared with a Mg support amount of 10g/L and varied Sr support amounts. Furthermore, catalysts were prepared with a Mg support amount of 15g/L and varied Sr support amounts. In these catalysts as well, the total Pt support amount is 3.5g/L, and the total Rh support amount is 0.106g/L.

[0305] Furthermore, catalysts were prepared by the same method and under the same conditions as in Example **1'**, except that aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate,

3NSDOCID: <EP 1127603A1 I >

strontium acetate and magnesium acetate were weighed and mixed so that the Pt support amount was 3.0g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Sr support amount was 10g/L and the Mg support amount was varied to prepare mixed solutions.

[0306] The NO_x purification ratios of the catalysts having varied support amounts of Mg and Sr were measured in the same manner as in the previously described evaluation test when the catalysts were fresh, after the SO_2 treatment and after the regeneration treatment. Figure **33** shows the results when the Mg support amount was 5g/L. Figure **34** shows the results when the Mg support amount was 10g/L. Figure **35A** shows the results when the Mg support amount was 15g/L. Figure **35B** shows the results when the Mg support amount was varied and the Sr support amount was 10g/L.

[0307] According to Figure **33**, in the Mg support amount of 5g/L, when the Sr support amount is 15g/L, the NO_x purification ratio after regeneration is highest, and the regeneration ratio of the NO_x purification ratio from SO_2 poisoning is high. According to Figure **34**, in the Mg support amount of 10g/L, when the Sr support amount is 10g/L, the NO_x purification ratio after regeneration is highest, and the regeneration ratio of the NO_x purification ratio from SO_2 poisoning is high. Also when the Sr support amount is 5g/L, the regeneration ratio of the NO_x purification ratio from SO_2 poisoning is high. According to Figure **35A**, when the Mg support amount is 15g/L, the regeneration ratio of the NO_x purification ratio from SO_2 poisoning is high in any Sr support amount of 5g/L to 15g/L. According to Figure **35B**, in the Sr support amount of 10g/L, when the Mg support amount is about 10g/L, the NO_x purification ratios after SO_2 treatment and after regeneration are high.

[0308] Thus, when Sr and Mg are used together with Ba and K, even if the Sr support amount is small, the regeneration ratio of the NO_x purification ratio from sulfur poisoning can be high.

[0309] Furthermore, for the comparative catalyst (which has been described in the above item of Ba-K-Sr based NO_x storage material), the NO_x purification ratio when the catalyst is fresh is 72%, the NO_x purification ratio after the SO_2 treatment is 41%, and the NO_x purification ratio after the regeneration treatment is 63%. Therefore, when K, Sr and Mg, in addition to Ba, are supported, all the NO_x purification ratios when the catalyst is fresh, after the SO_2 treatment and after the regeneration treatment are higher than those of the comparative catalyst, which contains only Ba as the NO_x storage material.

[0310] Figure **36** shows the results of measurement of the NO_x purification ratios of the catalysts having varied support amounts of Mg and Sr and the comparative catalyst after the heat deterioration treatment as previously described. The dotted broken line in Figure **36** indicates the NO_x purification ratio of the comparative catalyst. The space velocity was 25000h^{-1}. According to Figure **36**, when Sr and Mg are used in addition to Ba and K, the heat resistance of the catalyst is improved. This is advantageous for regeneration. However, too excessive support amounts of Sr and Mg may be disadvantageous for improving the heat resistance.

[0311] The above results indicate that when the Sr support amount is 8 to 20g/L (preferably, 8 to 15g/L) and the Mg support amount is 8 to 12g/L (preferably, 8 to 11g/L), the sulfur poisoning resistance, and the heat resistance and the regeneration properties from sulfur poisoning are good.

[0312] Figure **37** schematically shows the state of the presence in the catalytic layer of the Ba-K-Sr-Mg based NO_x storage material. It seems that a part of Ba and a part of Sr supported in the inner and outer coating layers form a compound (a mixed oxide or a double salt) constituted by Ba and Sr. It seems that a part of Ba and a part of Mg come close and are combined to be nearly amorphous. It seems that K is not combined with or not be compatible with Ba, Sr or Mg, and is dispersed around the Ba-Sr compound or the Ba-Mg coexisting substance.

[0313] It seems that the Ba-Sr compound (hereinafter, referred to as a double compound, if necessary) is less susceptible to sulfur poisoning than Ba alone, so that deterioration of the NO_x absorption ability can be suppressed. It seems that the Ba-Mg coexisting substance suppresses sulfur poisoning of Ba (production of barium sulfate) than Ba alone, so that deterioration of the NO_x absorption ability can be suppressed. It seems that K is relatively highly reactive with sulfur, so that when K surrounds the Ba-Sr compound or the Ba-Mg coexisting substance and prevents the Ba-Sr compound or the Ba-Mg coexisting substance from being sulfur-poisoned.

[Support amount of K]

[0314] The effect of the K support amount on the sulfur poisoning resistance, the regeneration properties from sulfur poisoning, and the heat resistance was examined.

[0315] More specifically, aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, strontium acetate, and magnesium acetate were weighed and mixed so that the Pt support amount was 6.5g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the Sr support amount was 10g/L, and the Mg support amount was 10g/L and the K support amount was 2g/L, 6g/L, 15g/L and 30g/L to prepare solutions for impregnation.

[0316] γ-alumina, Ce-Zr-Sr mixed oxide ($CeO_2 \cdot ZrO_2 \cdot SrO$ mixed oxide, the mass ratio of the three elements of Ce:Zr:Sr = 75:25:1)and an alumina binder were weighed and mixed so that the support amount of γ-alumina was 160g/L and the support amount of the Ce-Zr-Sr mixed oxide was 160g/L, and the support amount of the binder was 30g/L.

SPOCID: <EP 1127603A1 >

Then, ion exchanged water was added thereto to prepare slurry.

[0317] A honeycomb carrier was wash-coated with a half amount of the slurry, and dried and calcined to form an inner coating layer. Then, the inner coating layer was wash-coated with the other half of the amount of the slurry, and dried and calcined in the same manner to form an outer coating layer. Thereafter, the inner coating layer and the outer coating layer were impregnated with each of the above obtained solutions and dried and calcined so that catalysts having different K support amounts were obtained.

[0318] The NO_x purification ratios of the catalysts when the catalysts were fresh, after the SO_2 treatment, and after the regeneration treatment after the SO_2 treatment were measured in the same manner as the NO_x purification ratios described above. In this case, the temperature at which the NO_x purification ratios were measured (the gas temperature at the inlet of the catalyst) was 350°C. Figure **38** shows the results. Furthermore, the NO_x purification ratios after the heat deterioration treatment were measured in the same manner as the NO_x purification ratios described above. Figure **39** shows the results when the temperature at which the NO_x purification ratios were measured (the gas temperature at the inlet of the catalyst) was 350°C. Figure **40** shows the results when the temperature at which the NO_x purification ratios were measured was 450°C.

[0319] According to Figure **38**, the NO_x purification ratio when the catalyst is fresh is high when the K support amount is 2g/L and 6g/L. However, when the amount is increased, such as 15g/L and 30g/L, the purification ratio is decreased. The results indicate that it is not preferable that the K support amount is 15g/L or more.

[0320] The NO_x purification ratio after SO_2 treatment is at the peak at a K support amount of 6g/L, and the amount is further increased, the purification ratio is decreased. This decrease corresponds to the decrease of the NO_x purification ratio when the catalyst is fresh, and a decrease of the NO_x purification ratio due to sulfur poisoning is small. This indicates that K is effective for improving the sulfur poisoning resistance.

[0321] On the other hand, when the K support amount is 2g/L, the NO_x purification ratio after SO_2 treatment is low, but the NO_x purification ratio after regeneration treatment is high. Therefore, it is preferable that the K support amount is 2g/L or more.

[0322] According to Figure **39** (the NO_x purification ratio after heat deterioration treatment at a measurement temperature of 350°C), the NO_x purification ratio is at the peak in a K support amount of 6g/L. This indicates that K is effective for improving the heat resistance of the catalyst. When the amount is increased, such as 15g/L and 30g/L, the purification ratio after heat deterioration treatment is decreased. This seems to correspond to the decrease of the NO_x purification ratio when the catalyst is fresh (see Figure **38**). Such an effect of K on the heat resistance can be seen in Figure **40** (the NO_x purification ratio after heat deterioration treatment at a measurement temperature of 450°C), although it is not significant.

[0323] The results above indicate that it is preferable that the K support amount is 2 to 15g/L, more preferably 2 to 12g/L, even more preferably 4 to 10g/L.

[0324] Other examples for examining the effect of the K support amount on the performance of the catalyst will be described.

[0325] Catalysts were prepared by the same method and under the same conditions as in Example 1' described above, except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate and potassium acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the Ba support amount was 30g/L and the K support amount was 0g/L, 2g/L, 4g/L, 6g/L, 8g/L, 10g/L, and 30g/L to prepare mixed solutions, and these mixed solutions were used for impregnation.

[0326] The catalysts were heated in an ambient atmosphere at 900°C for 24 hours. Thereafter, each catalyst was attached to a fixed floor flow-through reaction evaluation apparatus, and first a simulated exhaust gas having a lean air-fuel ratio (gas composition **A** in Table **1**) was passed through the catalyst until the NO_x purification ratio became stable. Then, the simulated exhaust gas with the gas composition switched to one having a rich air-fuel ratio (gas composition **B** in Table **3**) was passed through the catalyst. Three minutes later, the gas composition was switched again to the lean air-fuel ratio (gas composition **A**), and for 130 seconds from this point of switching, the NO_x purification ratio (lean NO_x purification ratio) was measured. The temperature of the catalyst and the temperature of the simulated exhaust gas were 350°C. The space velocity **SV** was 25000h^{-1}.

[0327] The catalysts were heated in an ambient atmosphere at 900°C for 24 hours as in the case of measurement of the NO_x purification ratio. Thereafter, each catalyst was attached to a fixed floor flow-through reaction evaluation apparatus, and first a simulated exhaust gas having a lean air-fuel ratio (gas composition **A**) was passed through the catalyst until the NO_x purification ratio became stable. Then, the simulated exhaust gas with the gas composition switched to one having a rich air-fuel ratio (gas composition **B**) was passed through the catalyst. Three minutes later, the gas composition was switched again to the lean air-fuel ratio (gas composition **A**), and then three minutes later, the gas composition was switched again to the rich air-fuel ratio (gas composition **B**). For 130 seconds from this point of switching, the HC purification ratio was measured. The temperature of the catalyst and the temperature of the simulated exhaust gas were 350°C. The space velocity **SV** was 25000h^{-1}.

[0328] Figure **41** shows the results. According to Figure **41**, when the K support amount is 2g/L or more, the NO_x

3NSDOCID: <EP_____1127603A1_I_>

purification ratio exceeds 70%, and until 10g/L, the NO_x purification ratio is gradually increased. However, when the K support amount is more than 10g/L, the NO_x purification ratio is not further improved.

[0329] Furthermore, there is a tendency that the larger the K support amount is, the lower the HC purification ratio is. In particular, until the K support amount is 6g/L, the HC purification is kept at least 95%. However, at more than 6g/L, the HC purification is dropped drastically to the 80% range. This seems to be because more K is disposed around the precious metals in a K support amount of more than 6g/L, so that HC is inhibited from coming close to the precious metals.

[0330] Therefore, in order to balance between the NO_x purification properties at lean ratios and the HC-form-chemical conversion at stoichiometric or rich ratios, it is preferable that the K support amount is 2 to 6g/L. The results of this measurement are from the examples that contain no Sr or Mg as the NO_x storage materials. However, it seems that regarding the K support amount, the same can be true for the examples that contain Sr and Mg.

[Support amount of Ba]

[0331] The effect of the Ba support amount on the performance of the catalyst was examined.

[0332] Catalysts were prepared by the same method and under the same conditions as in Example **1'** described above, except that aqueous solutions of dinitrodiamine platinum nitrate, barium acetate, and potassium acetate were weighed and mixed so that the Pt support amount was 6.0g/L, the K support amount was 6g/L, the Ba support amount was 5g/L, 10g/L, 15g/L, 20g/L, 30g/L, 40g/L and 50g/L to prepare mixed solutions, and these mixed solutions were used for impregnation.

[0333] The NO_x purification ratios of the catalysts were measured under the same conditions in the same method. More specifically, the catalysts were heated in an ambient atmosphere at 900°C for 24 hours. Thereafter, each catalyst was attached to a fixed floor flow-through reaction evaluation apparatus, and the air-fuel ratio was switched from a lean air-fuel ratio (gas composition **A**), to a rich air-fuel ratio (gas composition **B**) and to the lean air-fuel ratio (gas composition **A**), and for 130 seconds from this point of switching, the NO_x purification ratio (lean NO_x purification ratio) was measured. The temperature of the catalyst and the temperature of the simulated exhaust gas were 350°C. The space velocity **SV** was 25000h^{-1}.

[0334] Figure **42** shows the results. According to Figure **42**, as the Ba support amount is larger, the NO_x purification ratio is improved significantly, when the Ba support amount is from 5g/L to 15g/L. When the Ba support amount is from 15g/L to 30g/L, the degree of improvement of the NO_x purification ratio becomes smaller. When the Ba support amount is 30g/L, the NO_x purification ratio is at the peak. After that, even if the Ba support amount is increased, the NO_x purification ratio about equal to that in a Ba support amount of 30g/L only can be achieved. Therefore, it cannot be expected that the NO_x purification ratio is improved even if the Ba support amount is increased to more than 30g/L. It is preferable that the mass ratio of the Ba support amount to the K support amount is about 5 to 15.

[Effect of support amount of Pt]

[0335] Aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, strontium acetate, and magnesium acetate were weighed and mixed so that the Pt support amount was 6.5g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, the K support amount was 6g/L, the Sr support amount was 10g/L, and the Mg support amount was 10g/L to prepare a mixed solution for impregnation.

[0336] γ-alumina, a Ce-Zr-Sr mixed oxide (CeO_2·ZrO_2·SrO mixed oxide, the mass ratio of the three elements of Ce:Zr:Sr = 75:25:1)and an alumina binder were weighed and mixed so that the support amount of γ-alumina was 160g/L and the support amount of the Ce-Zr-Sr mixed oxide was 160g/L, and the support amount of the binder was 30g/L. Then, ion exchanged water was added thereto to prepare slurry.

[0337] A honeycomb carrier was wash-coated with a half amount of the slurry, and dried and calcined to form an inner coating layer. Then, the inner coating layer was wash-coated with the other half of the amount of the slurry, and dried and calcined to form an outer coating layer. Thereafter, the inner coating layer and the outer coating layer were impregnated with the above obtained solution, and dried and calcined so that a catalyst having a Pt support amount of 6.5g was obtained.

[0338] Another catalyst was prepared by the same method and under the same conditions as in the catalyst having a Pt support amount of 6.5g/L, except that the Pt support amount was 3.5g/L.

[0339] The NO_x purification ratios of the catalysts having Pt support amounts of 3.5g/L and 6.5g/L when the catalysts were fresh, after SO_2 treatment, and after regeneration treatment were measured in the same manner as the NO_x purification ratios described above. In this case, the temperature at which the NO_x purification ratios were measured (the gas temperature at the inlet of the catalyst) was 350°C. The space velocity was 55000h^{-1}. Figure **43** shows the results together with the results of Example **1'**.

[0340] According to Figure **43**, for the catalyst having a Pt support amount of 6.5g/L, the NO_x purification ratio when

SDOCID: <EP 1127603A1 >

the catalyst is fresh is high, and the NO_x purification ratio after the SO_2 treatment and after the regeneration treatment are higher than those of Examples **1'** to **11'** (see Figure **26**). In particular, it is characteristic that the NO_x purification ratio after regeneration treatment is equal to that when the catalyst is fresh.

[0341] On the other hand, for the catalyst having a Pt support amount of 3.5g/L, the NO_x purification ratio after regeneration treatment is equal to that when the catalyst is fresh, but the NO_x purification ratios when the catalyst is fresh, after SO_2 treatment and after regeneration treatment are lower than those of the catalyst having a Pt support amount of 6.5g/L. This seems to be because the amount of Pt present close to Ba is small because of the small support amount of Pt, and therefore even if NO_x comes close to Ba, absorption and reduction of NO_x by an interaction between Ba and Pt cannot be achieved sufficiently.

[0342] Nest, the NO_x purification ratios of the catalysts having Pt support amounts of 3.5g/L and 6.5g/L when the catalysts were fresh and after heat deterioration treatment were measured in the same manner as the NO_x purification ratios described above. In this case, the temperature at which the NO_x purification ratios were measured (the gas temperature at the inlet of the catalyst) was two kinds of 350°C and 450°C. The space velocity was 55000h^{-1}. Figure **44** shows the results at 350°C together with the results of Example **1'**. Figure **45** shows the results at 450°C together with the results of Example **1'**.

[0343] According to Figures **44** and **45**, for the catalyst having a Pt support amount of 6.5g/L, the NO_x purification ratio after heat deterioration treatment is higher than those of Examples **1'** to **11'** (see Figures **27** and **28**). For the catalyst having a Pt support amount of 3.5g/L as well, it can be said that the heat resistance is higher, in view of that fact that the Pt support amount is smaller than that (about 6g/L) of Examples **1'** to **11'**.

[Order of impregnation of precious metal and NO_x storage material]

[0344] The effect of the order of impregnation of the precious metal and the NO_x storage material on the performance of the catalyst was examined.

[0345] As mixed solutions for impregnation, aqueous solutions of strontium acetate and magnesium acetate were weighed and mixed so that the Sr support amount was 10g/L and the Mg support amount was 10g/L to prepare a first solution for impregnation. Aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, and potassium acetate were weighed and mixed so that the Pt support amount was 6.5g/L, the Rh support amount was 0.1g/L, the Ba support amount was 30g/L, and the K support amount was 6g/L to prepare a second solution. On the other hand, inner and outer coating layers were formed of γ-alumina, a Ce-Zr-Sr mixed oxide and an alumina binder on a honeycomb carrier by the method and under the same conditions as above.

[0346] Then, the inner and the outer coating layers were impregnated with the first solution, and dried and calcined, followed by impregnation with the second solution, drying and calcining so that a catalyst was obtained. This catalyst is referred to as Mg and Sr earlier impregnation catalyst.

[0347] Furthermore, as mixed solutions for impregnation, aqueous solutions of barium acetate and magnesium acetate were weighed and mixed so that the Ba support amount was 30g/L and the Mg support amount was 10g/L to prepare a first solution for impregnation. Aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, strontium acetate, and potassium acetate were weighed and mixed so that the Pt support amount was 6.5g/L, the Rh support amount was 0.1g/L, the Sr support amount was 10g/L, and the K support amount was 6g/L to prepare a second solution. On the other hand, inner and outer coating layers were formed of γ-alumina, a Ce-Zr-Sr mixed oxide and an alumina binder on a honeycomb carrier by the method and under the same conditions as above.

[0348] Then, the inner and the outer coating layers were impregnated with the first solution, and dried and calcined, followed by impregnation with the second solution, drying and calcining so that a catalyst was obtained. This catalyst is referred to as Ba and Mg earlier impregnation catalyst.

[0349] The NO_x purification ratios of the two kinds of catalysts having different orders of impregnation when the catalysts were fresh, after SO_2 treatment and after regeneration treatment, and after heat deterioration treatment were measured in the same manner as the NO_x purification ratios described above. In this case, the temperature at which the NO_x purification ratios were measured (the gas temperature at the inlet of the catalyst) was 350°C. The space velocity was 55000h^{-1}. Figure **46** shows the results of measurement of the NO_x purification ratios when the catalysts were fresh, after SO_2 treatment and after regeneration treatment together with the results of Example **1'** and a simultaneously impregnated catalyst. Figure **47** shows the results of measurement of the NO_x purification ratio after heat deterioration treatment together with the results of Example **1'**and a simultaneously impregnated catalyst.

[0350] The simultaneously impregnated catalyst was a catalyst having a Pt support amount of 6.5g/L (the catalyst indicated as "Pt support amount of 6.5g/L" in Figures **31** to **33**) obtained by simultaneously impregnating the inner and the outer coating layers comprising of γ-alumina, a Ce-Zr-S mixed oxide and an alumina binder with aqueous solutions of dinitrodiamine platinum nitrate, rhodium nitrate, barium acetate, potassium acetate, strontium acetate and magnesium acetate.

[0351] According to Figure **46**, the Mg and Sr earlier impregnation catalyst and the Ba and Mg earlier impregnation

NSDOCID: <EP_____1127603A1_I_>

catalyst have slightly lower NO_x purification ratios when the catalysts are fresh and after regeneration treatment than those of the simultaneously impregnated catalyst. However, the NO_x purification ratios after SO_2 treatment thereof are higher. Furthermore, according to Figure **47**, the Mg and Sr earlier impregnation catalyst and the Ba and Mg earlier impregnation catalyst have slightly lower NO_x purification ratio after heat deterioration treatment than that of the simultaneously impregnated catalyst. However, when the Mg and Sr earlier impregnation catalyst is compared with the Ba and Mg earlier impregnation catalyst, the former has a higher NO_x purification ratio.

[0352] Therefore, when the inner and the outer coating layers should be impregnated with a large amount of solution, the solution can be divided into two for impregnation. In this case, it is preferable that the Sr solution is contained in the earlier impregnation solution, and the K solution is contained in the later impregnation solution.

[0353] The present invention can be applied not only to exhaust gases from automobile engines (lean burn engine or diesel engine), but also to industrial fixed engines. In this case, desired effects can be obtained by constituting the above-described embodiments. In this case, industrial engines refer to those utilized for air conditioning, for example, in buildings by heat exchange of heat of exhaust gases. In this case, when a heat exchanger is provided in the upstream of the catalyst, and when raising the temperature of the catalyst as in the above embodiments, the heat exchange efficiency is reduced by reducing the amount of water for heat exchange so that inhibition of raising the temperature can be prevented.

[0354] The invent ion may be embodied in other forms without departing from the spirit or essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not limiting. The scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

Claims

1. A catalyst for purifying an exhaust gas comprising: a catalytic metal that serves for oxidization of HC and CO in the exhaust gas containing oxygen and reduction of NO_x in said gas, and a mixed oxide comprising Ce, Zr and Sr.

2. The catalyst for purifying an exhaust gas of claim 1,
   wherein the catalytic metal is a precious metal.

3. The catalyst for purifying an exhaust gas of claim 1, comprising a NO_x storage material that absorbs NO_x in the exhaust gas in an oxygen-excessive atmosphere in which an oxygen concentration in the exhaust gas is high, and releases the absorbed NO_x by reduction of the oxygen concentration.

4. The catalyst for purifying an exhaust gas of claim 2, comprising a NO_x storage material that absorbs NO_x in the exhaust gas in an oxygen-excessive atmosphere in which an oxygen concentration in the exhaust gas is high, and releases the absorbed NO_x by reduction of the oxygen concentration.

5. A catalyst for purifying an exhaust gas, comprising:

   a carrier,
   an inner catalytic layer disposed on the carrier, comprising:

      a precious metal,
      a NO_x storage material that absorbs NO_x in the exhaust gas in an oxygen-excessive atmosphere in which an oxygen concentration in the exhaust gas is high, and releases the absorbed NO_x by reduction of the oxygen concentration, and
      a mixed oxide containing Ce, Zr, and Sr, and

   an outer catalytic layer disposed on the inner catalytic layer, comprising:

      a precious metal, and
      zeolite.

6. The catalyst for purifying an exhaust gas of any one of claims 1 to 5, wherein the mixed oxide contains Sr in an amount of 0.5 to 2.0 mass percent in terms of SrO.

7. A method for purifying an exhaust gas, comprising:

disposing the catalyst for purifying an exhaust gas of claim 1 in a site in an exhaust gas channel on which a temperature of the catalyst is at least 800°C; and
contacting the exhaust gas flowing through the exhaust gas channel with the catalyst for purifying the exhaust gas.

INSPOCID: <EP 1127603A1 >

FIG. 1

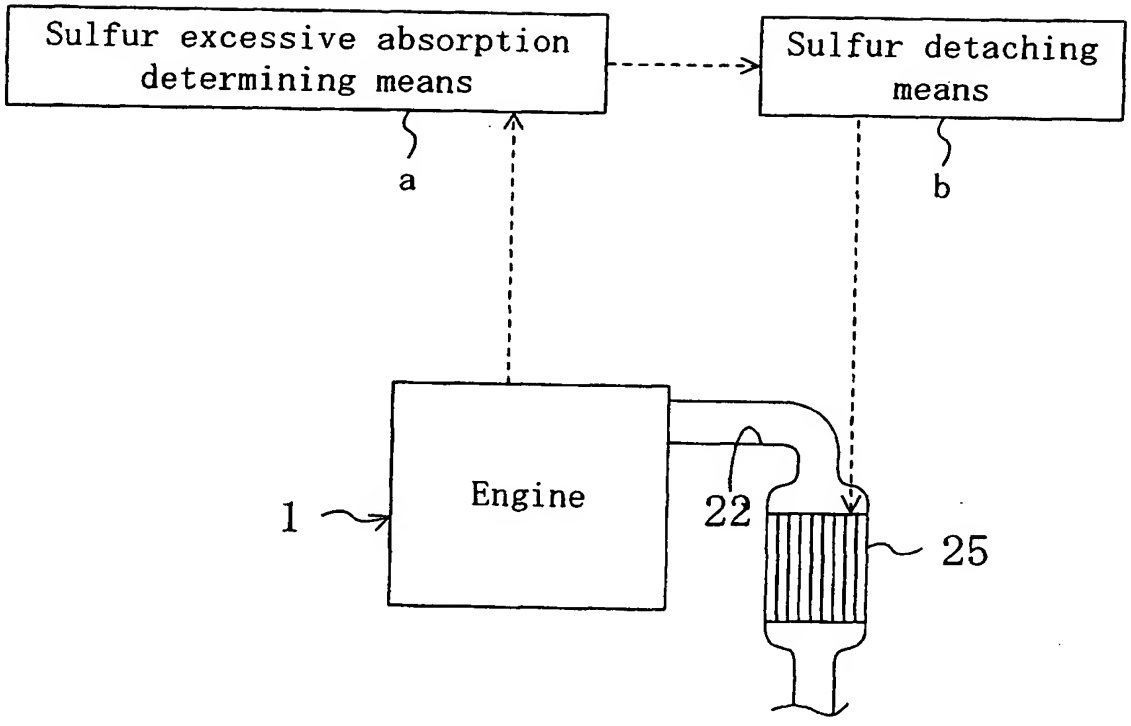
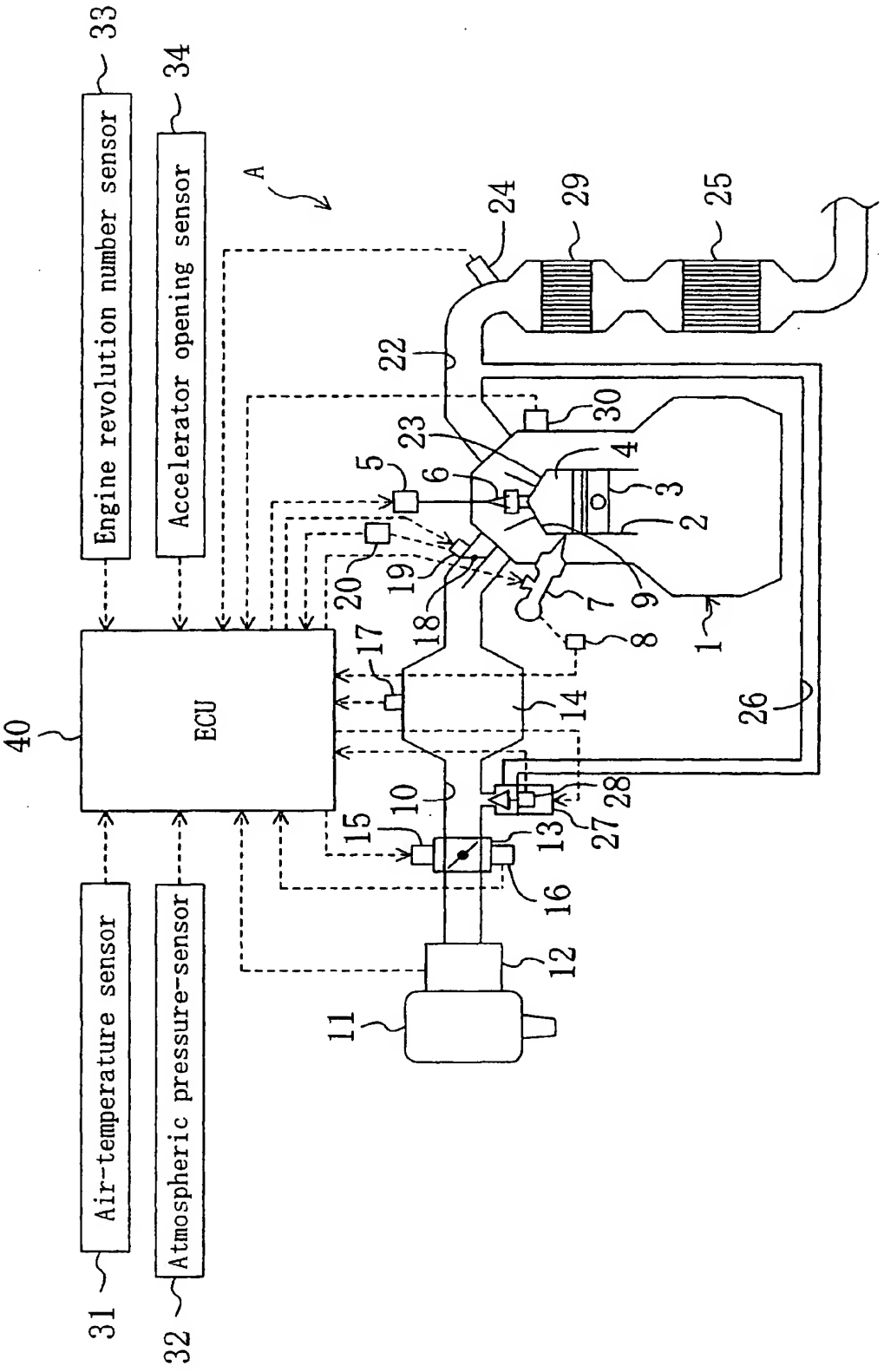

Sulfur excessive absorption determining means
Sulfur detaching means
a
b
Engine
1
22
25

FIG. 2



NSDOCID: <EP 1127603A1 I >

FIG. 3

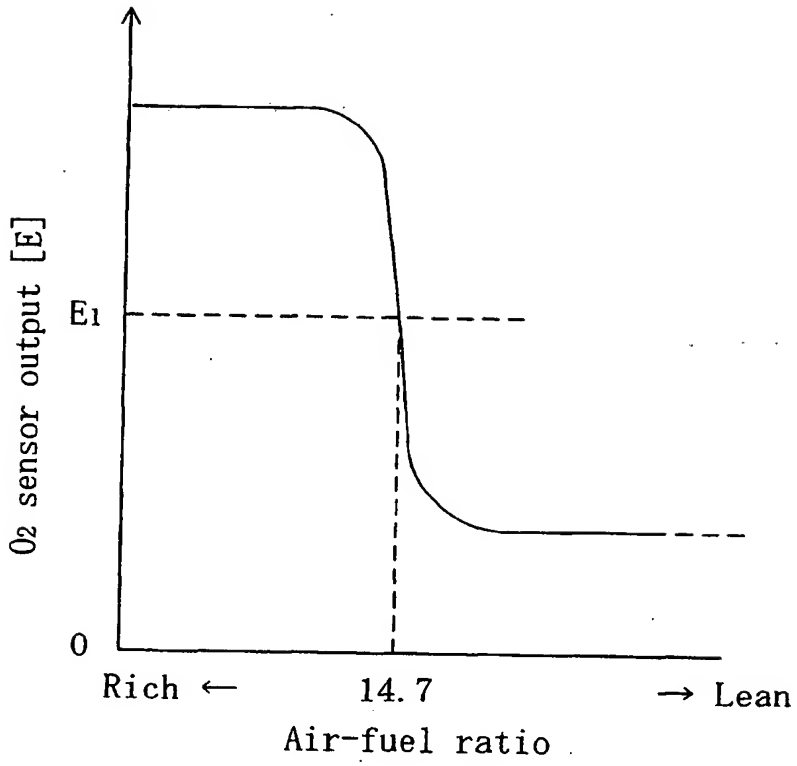
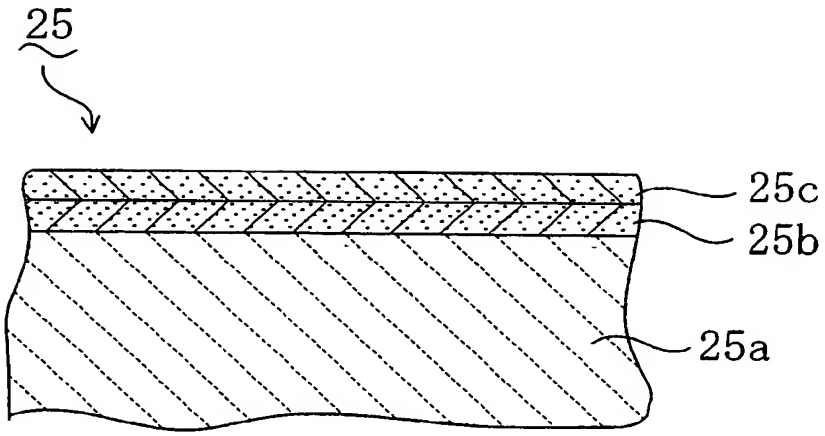


FIG. 4



...NSDOCID: <EP 1127603A1 >

FIG. 5

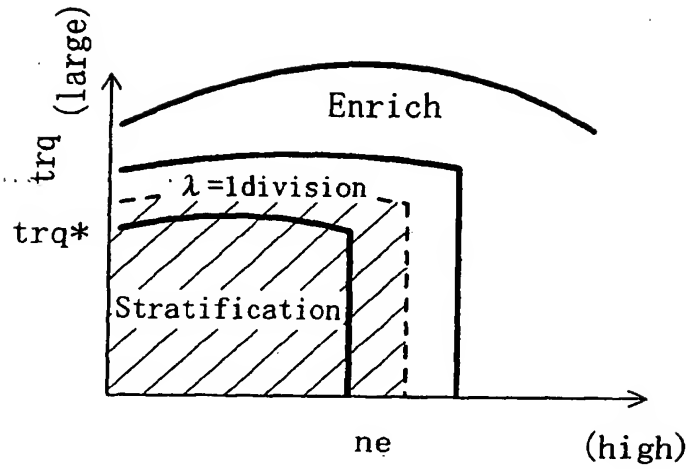
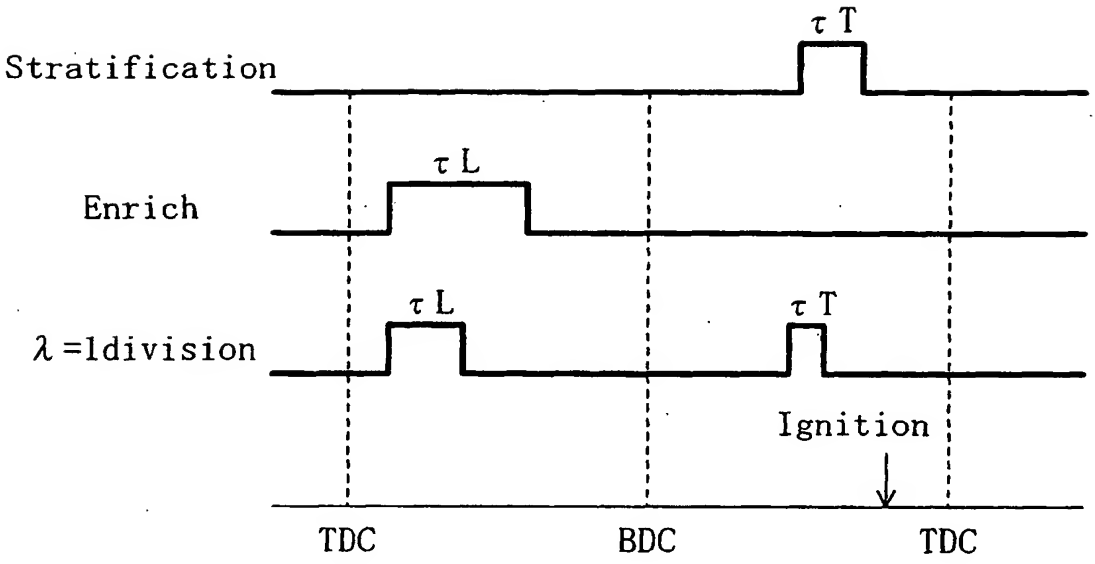


FIG. 6



NSDOCID: <EP 1127603A1 I >

FIG. 7A

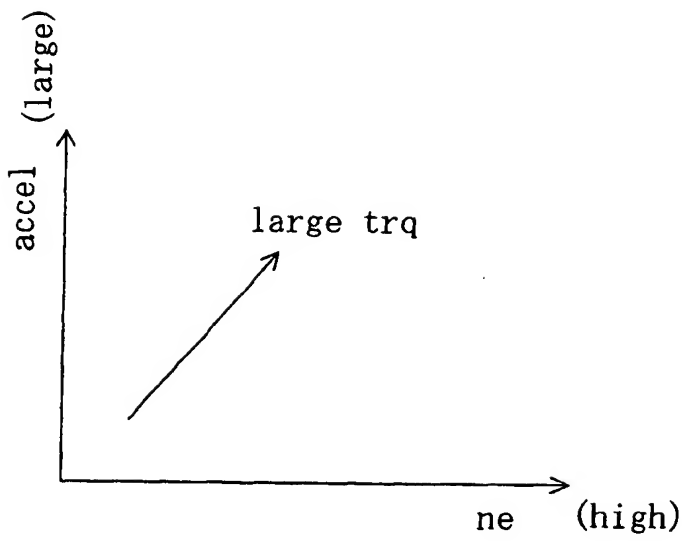

accel (large)
large trq
ne (high)

FIG. 7B

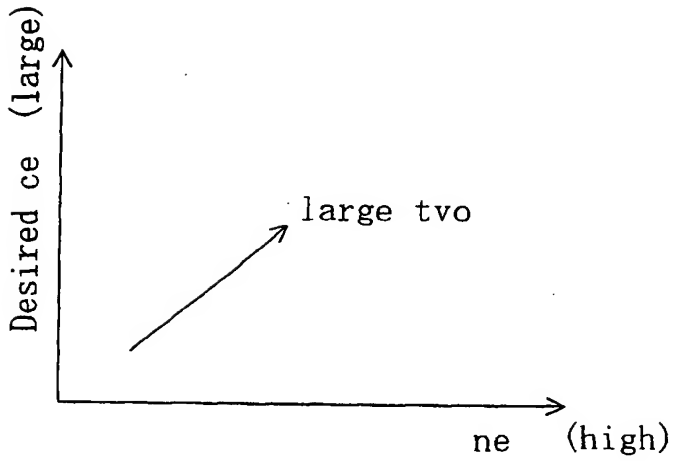

Desired ce (large)
large tvo
ne (high)

FIG. 8

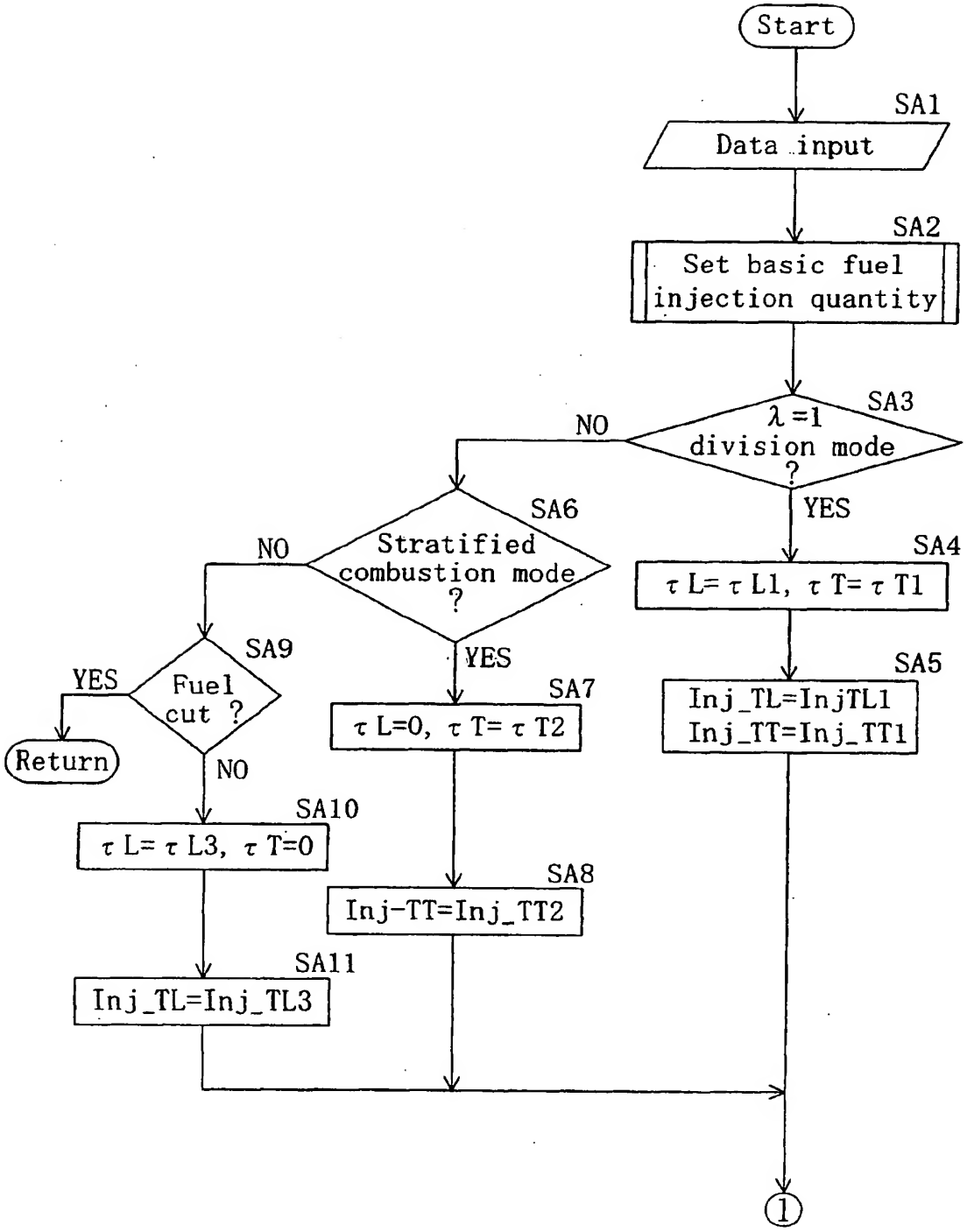


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FIG. 9

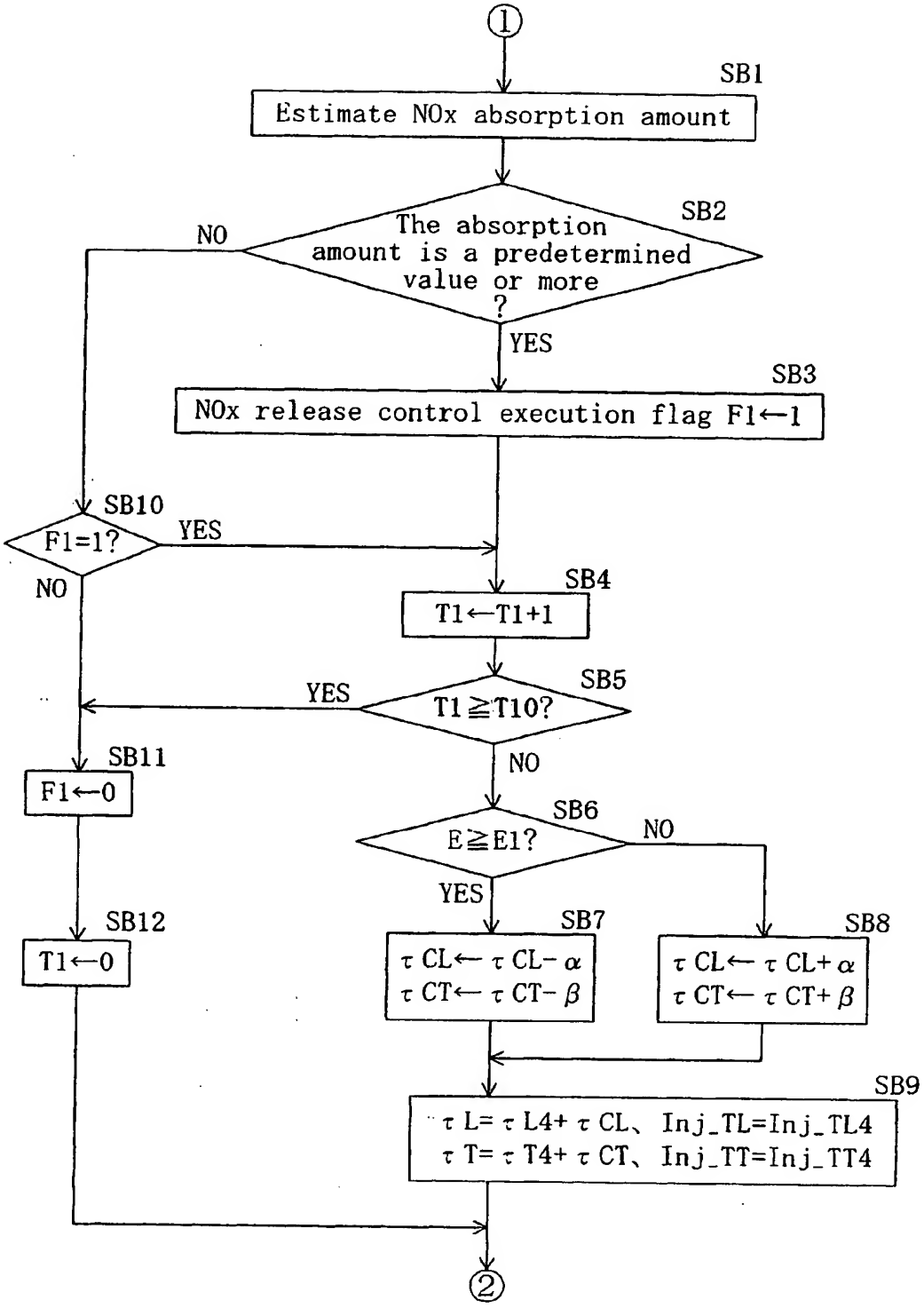
①
SB1
Estimate NOx absorption amount
SB2
The absorption amount is a predetermined value or more ?
NO
YES
SB3
NOx release control execution flag F1←1
SB10
F1=1?
YES
NO
SB4
T1←T1+1
SB5
T1≧T10?
YES
NO
SB11
F1←0
SB6
E≧E1?
NO
YES
SB12
T1←0
SB7
τCL←τCL−α
τCT←τCT−β
SB8
τCL←τCL+α
τCT←τCT+β
SB9
τL=τL4+τCL、Inj_TL=Inj_TL4
τT=τT4+τCT、Inj_TT=Inj_TT4
②

FIG. 10

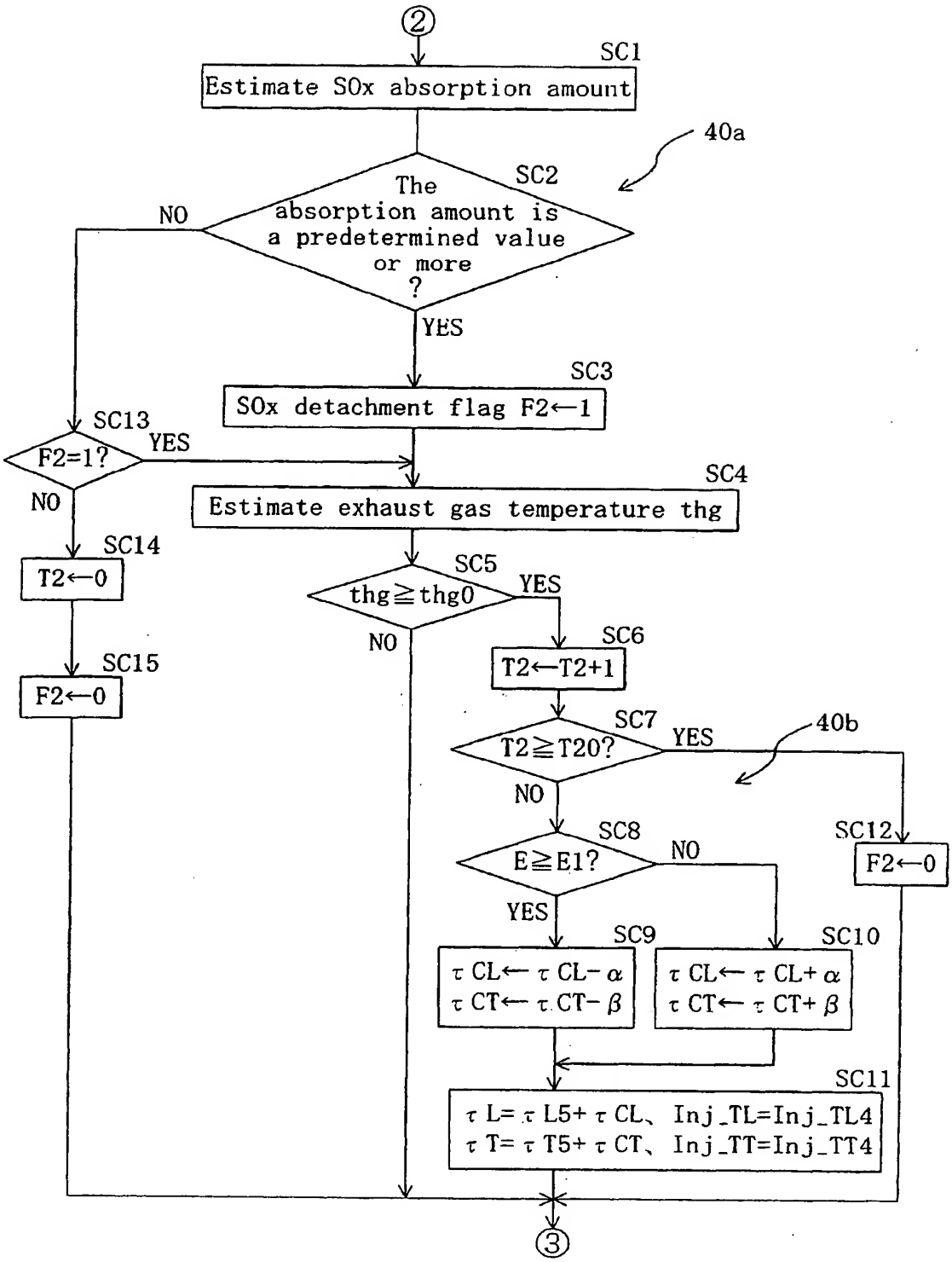

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FIG. 11

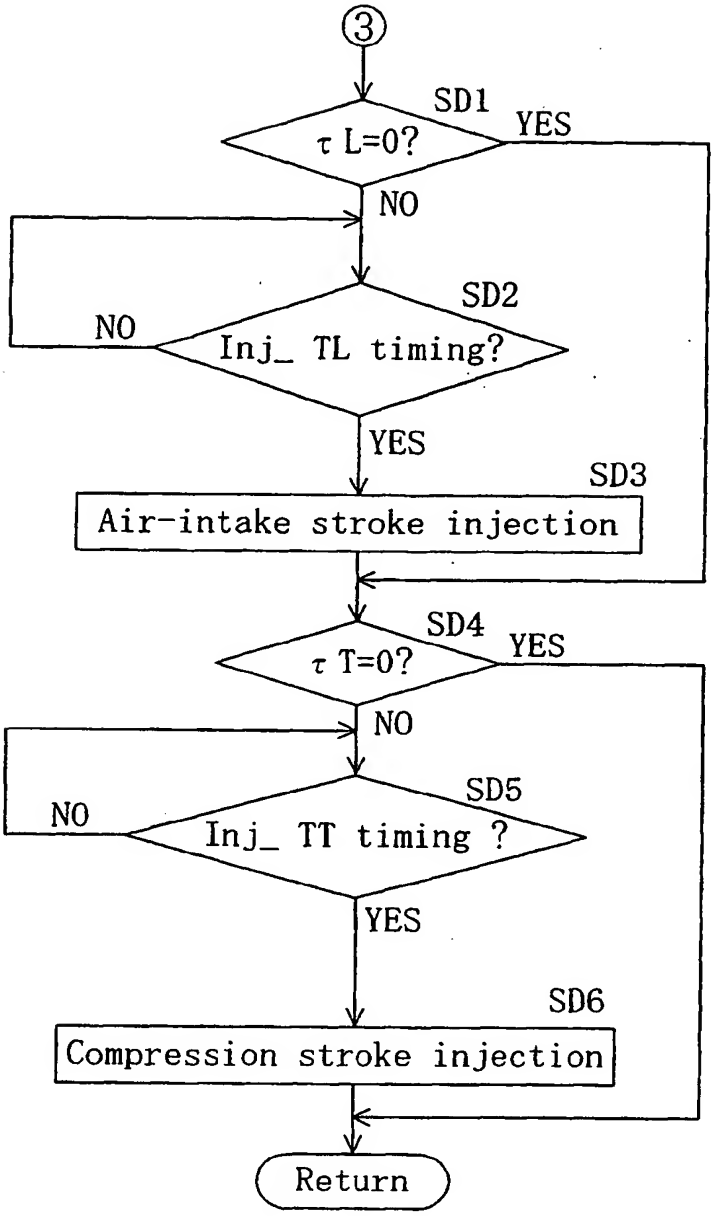
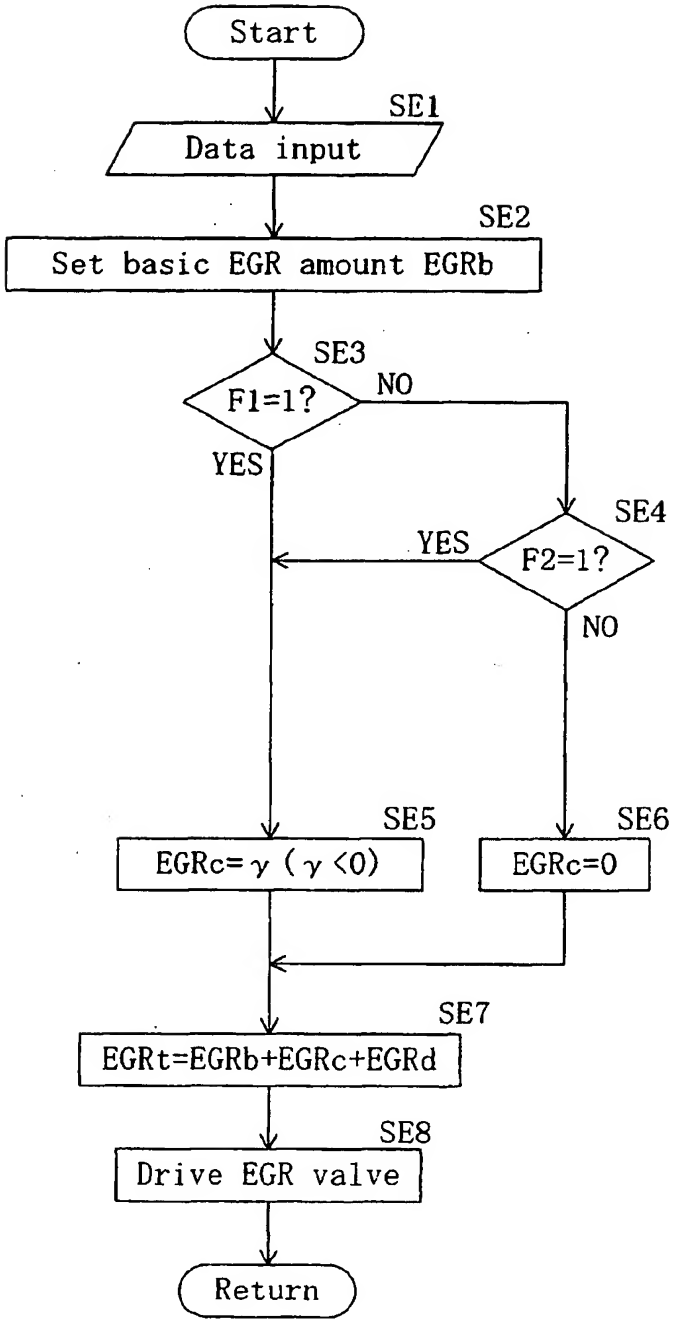

③
SD1
τ L=0?
YES
NO
SD2
NO
Inj_ TL timing?
YES
SD3
Air-intake stroke injection
SD4
τ T=0?
YES
NO
SD5
NO
Inj_ TT timing ?
YES
SD6
Compression stroke injection
Return

FIG. 12



NSDOCID: <EP 1127603A1 >

FIG. 13

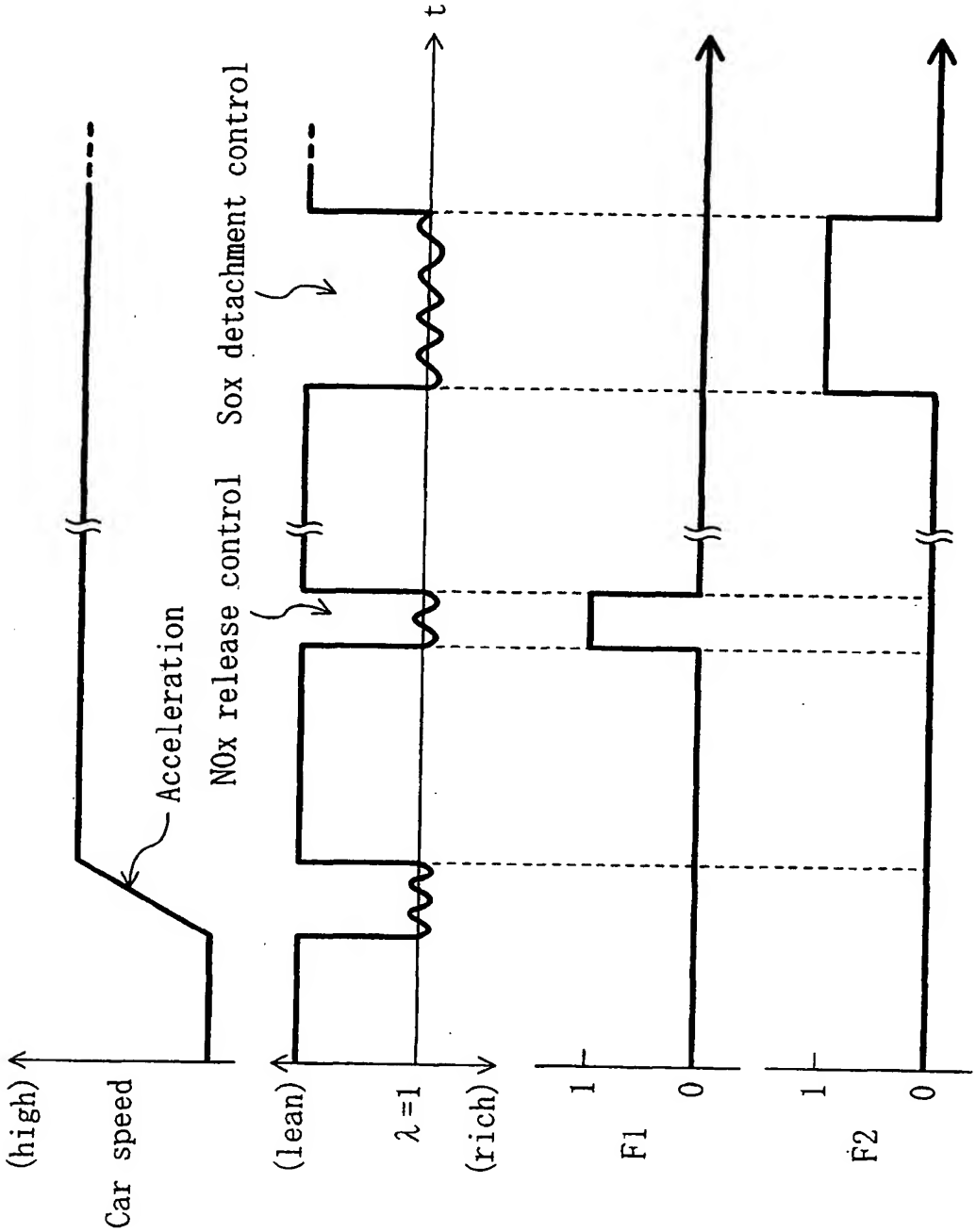

Acceleration
NOx release control
Sox detachment control
t
(high)
Car speed
(lean)
λ=1
(rich)
1
0
F1
1
0
F2

FIG. 14

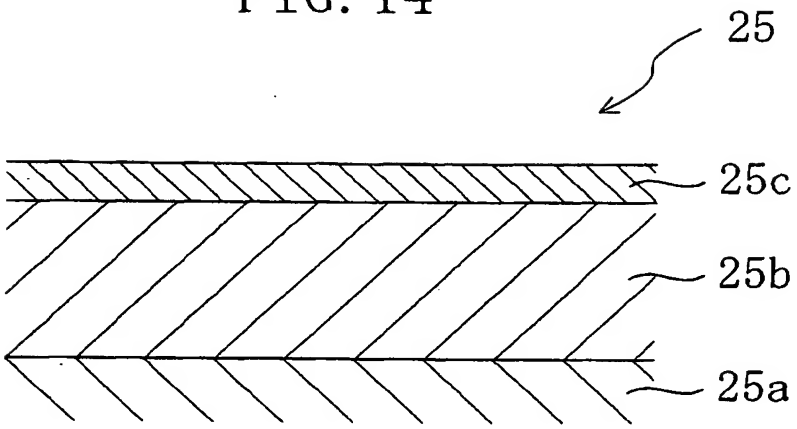


FIG. 15

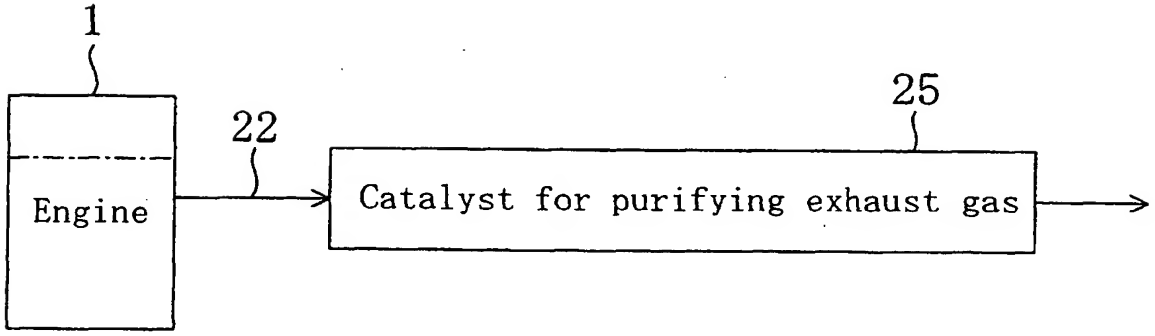


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FIG. 16

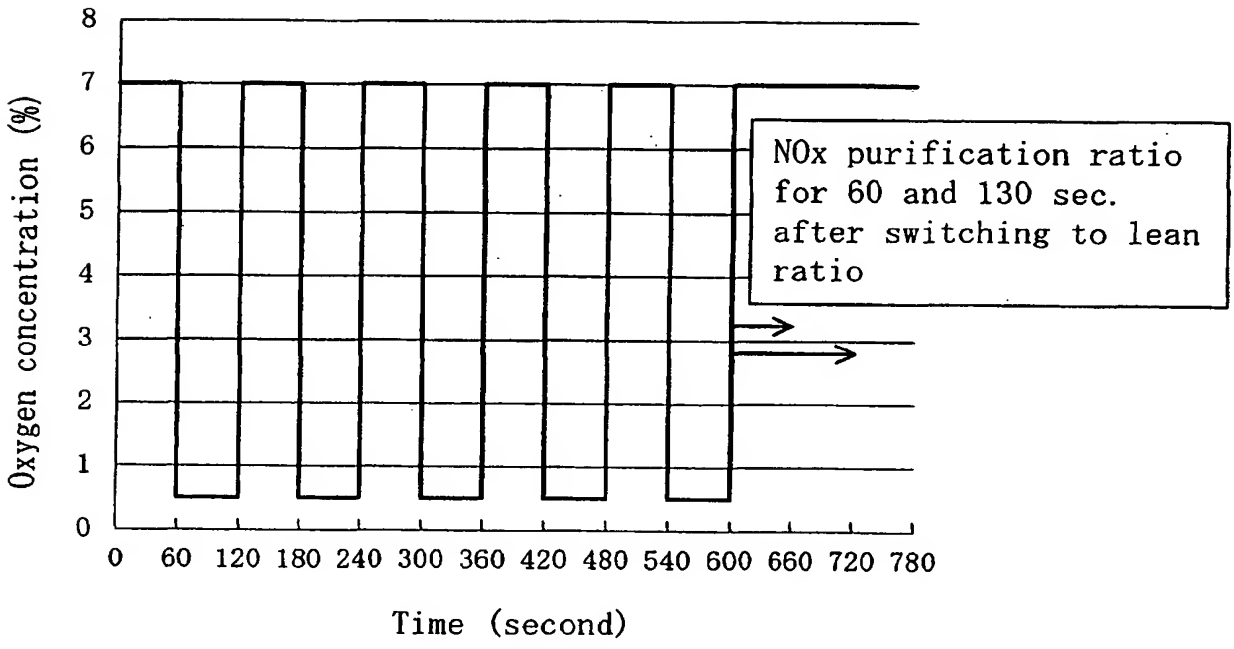
Oxygen concentration (%)
0
1
2
3
4
5
6
7
8
0 60 120 180 240 300 360 420 480 540 600 660 720 780
Time (second)
NOx purification ratio for 60 and 130 sec. after switching to lean ratio

FIG. 17

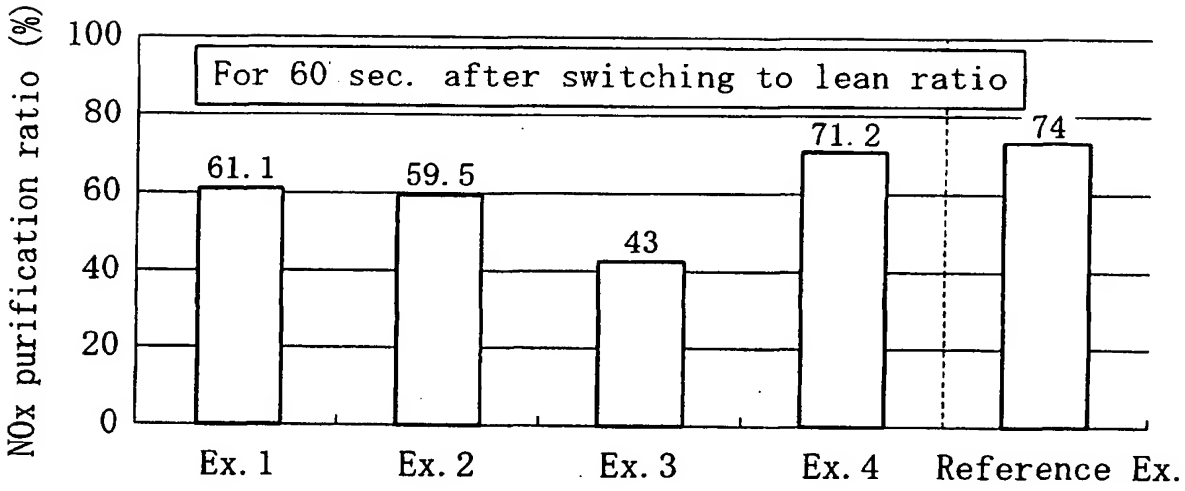

FIG. 18

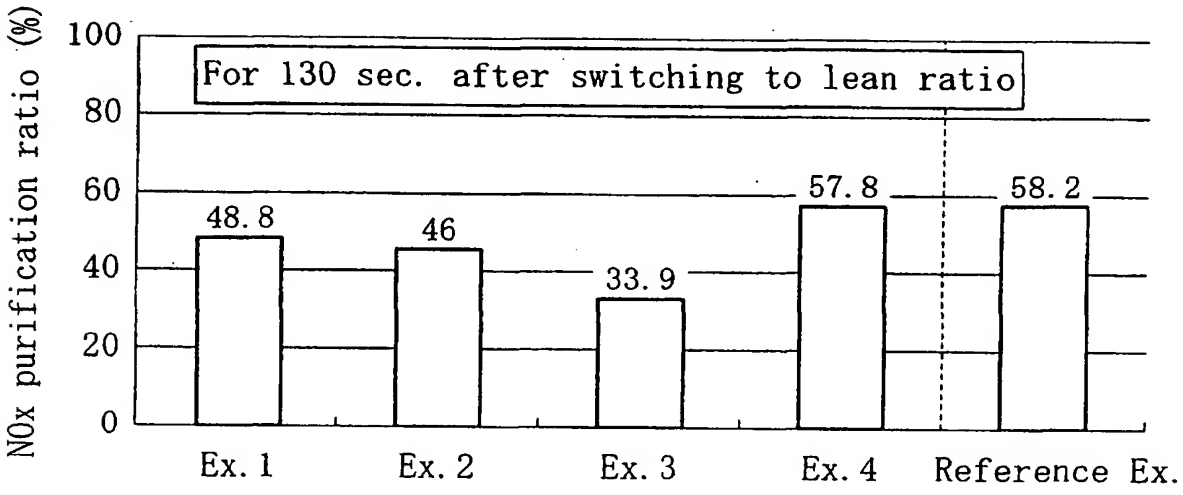

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FIG. 19

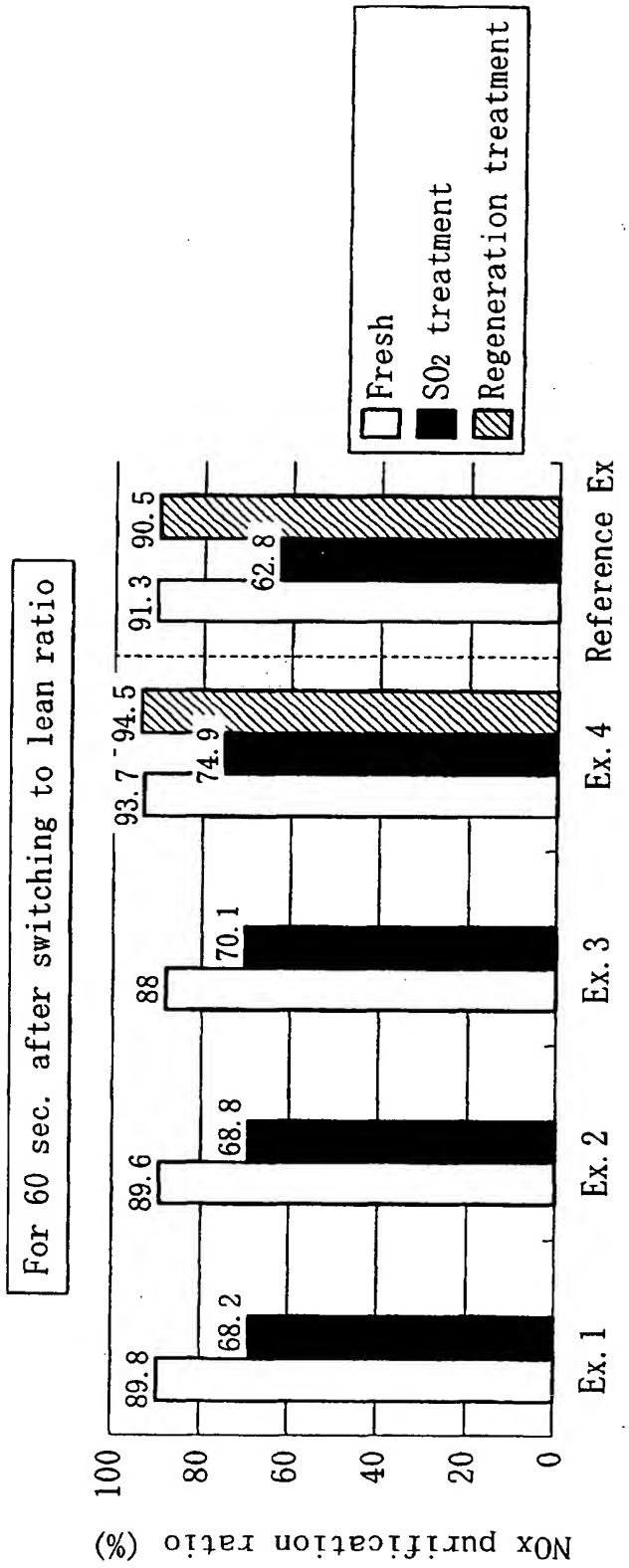
For 60 sec. after switching to lean ratio
Fresh
SO2 treatment
Regeneration treatment
NOx purification ratio (%)
100
80
60
40
20
0
89.8
68.2
89.6
68.8
88
70.1
93.7
74.9
94.5
91.3
62.8
90.5
Ex. 1
Ex. 2
Ex. 3
Ex. 4
Reference Ex

FIG. 20

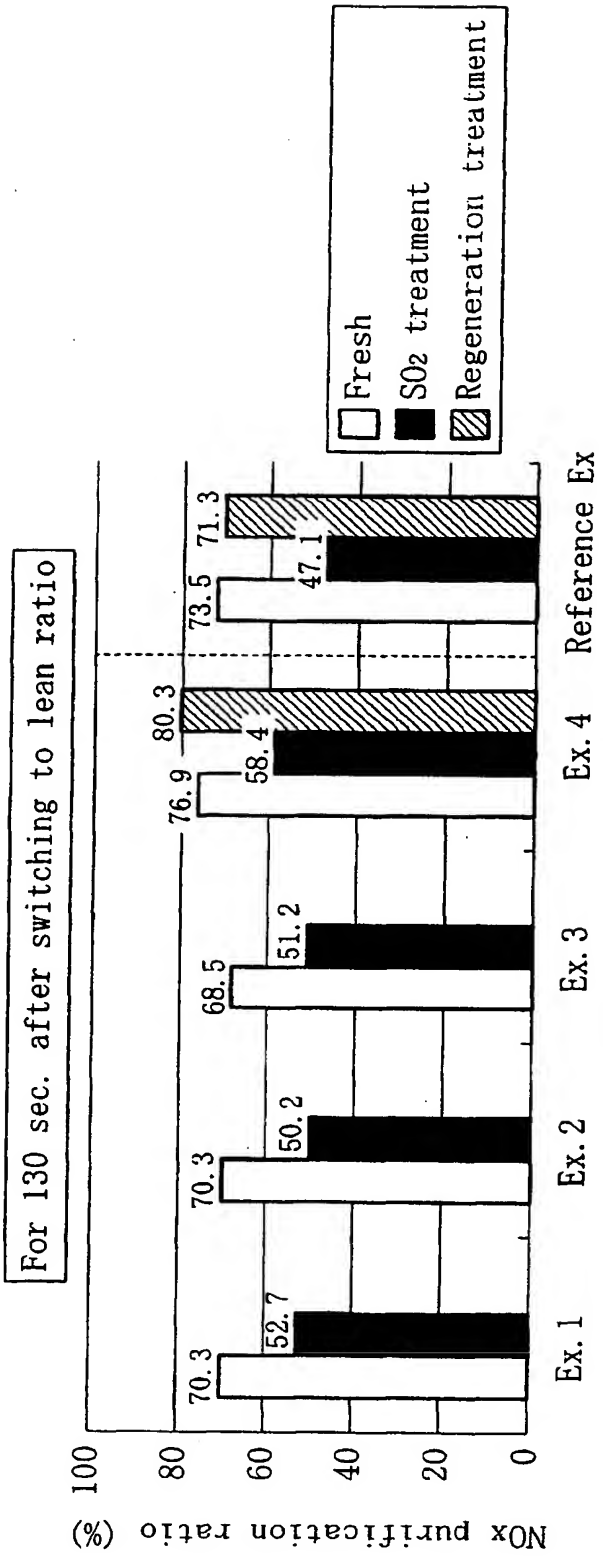

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FIG. 21

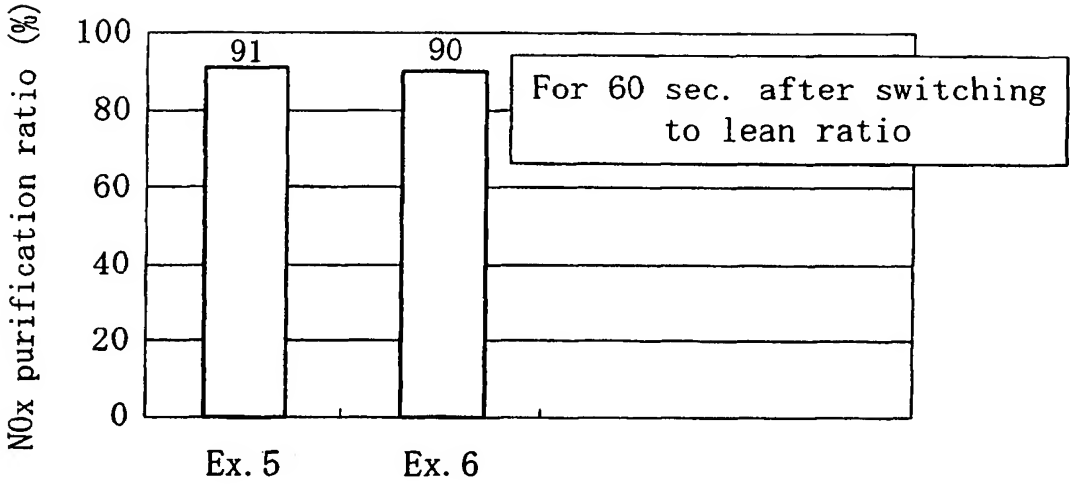
NOx purification ratio (%)
100
80
60
40
20
0
91
90
For 60 sec. after switching to lean ratio
Ex. 5
Ex. 6

FIG. 22

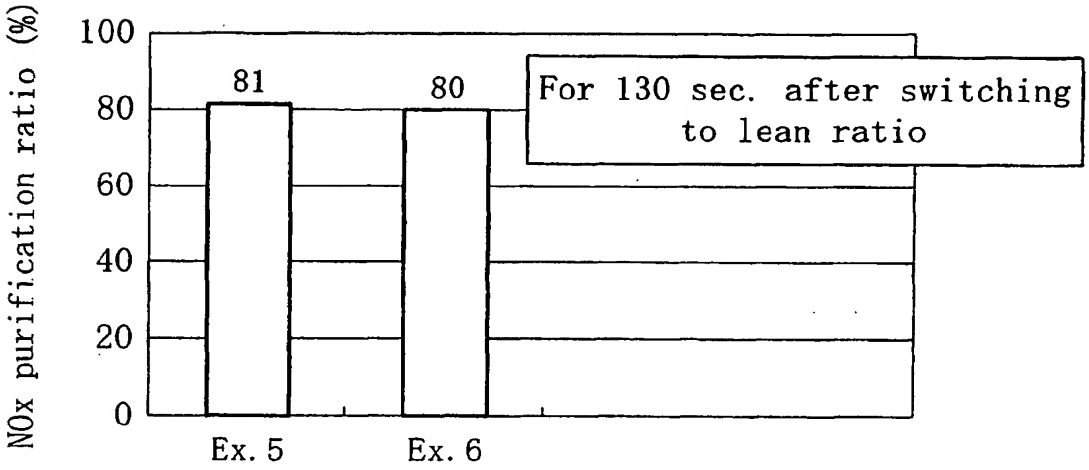
NOx purification ratio (%)
100
80
60
40
20
0
81
80
For 130 sec. after switching to lean ratio
Ex. 5
Ex. 6

FIG. 23

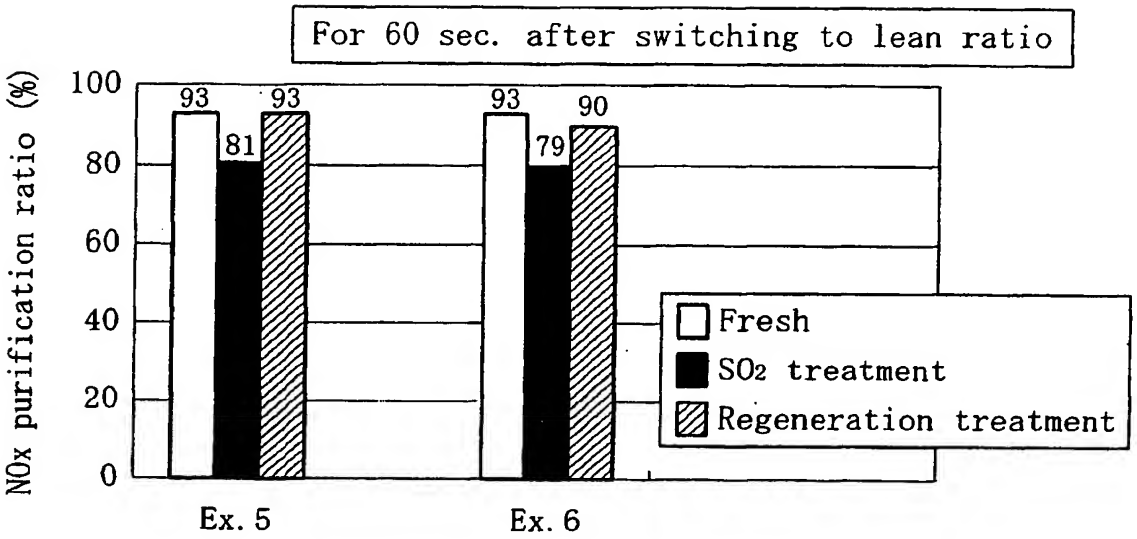

FIG. 24

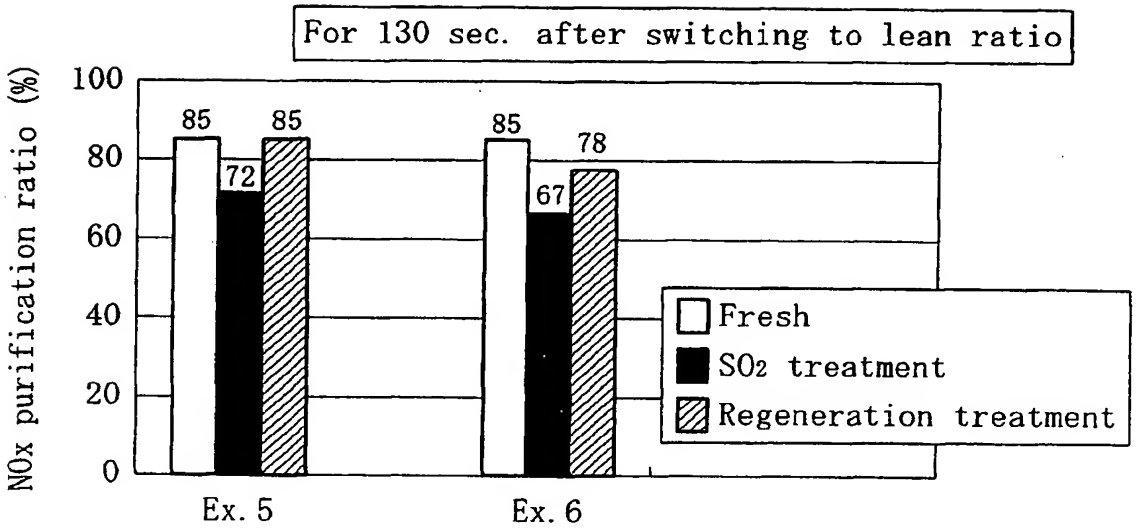

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FIG. 25

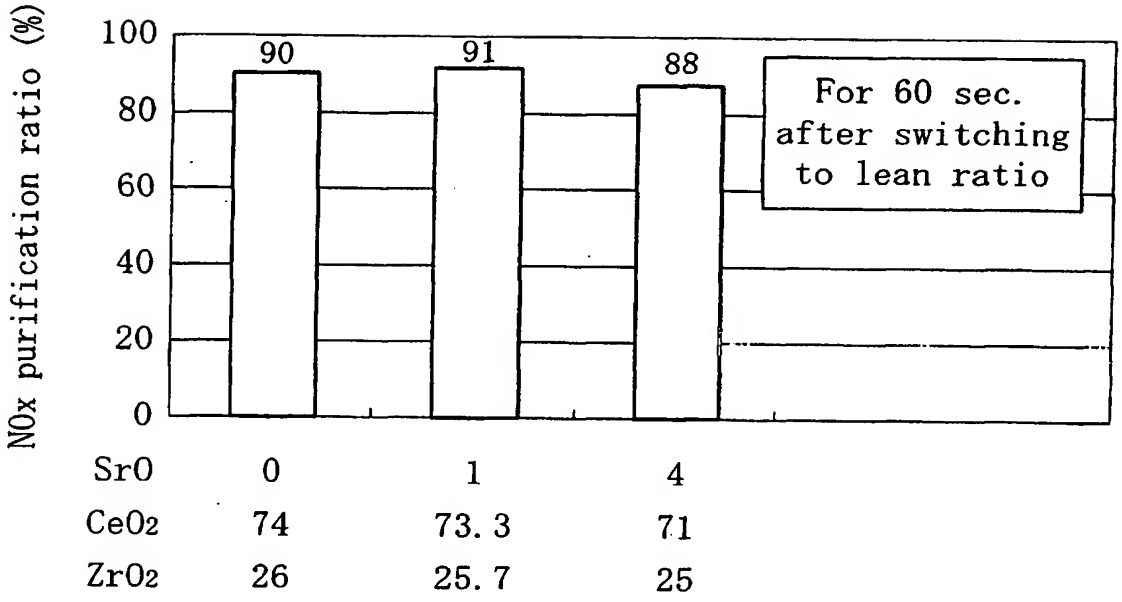
NOx purification ratio (%)
100
80
60
40
20
0
90
91
88
For 60 sec. after switching to lean ratio
SrO 0 1 4
CeO2 74 73.3 71
ZrO2 26 25.7 25

FIG. 26

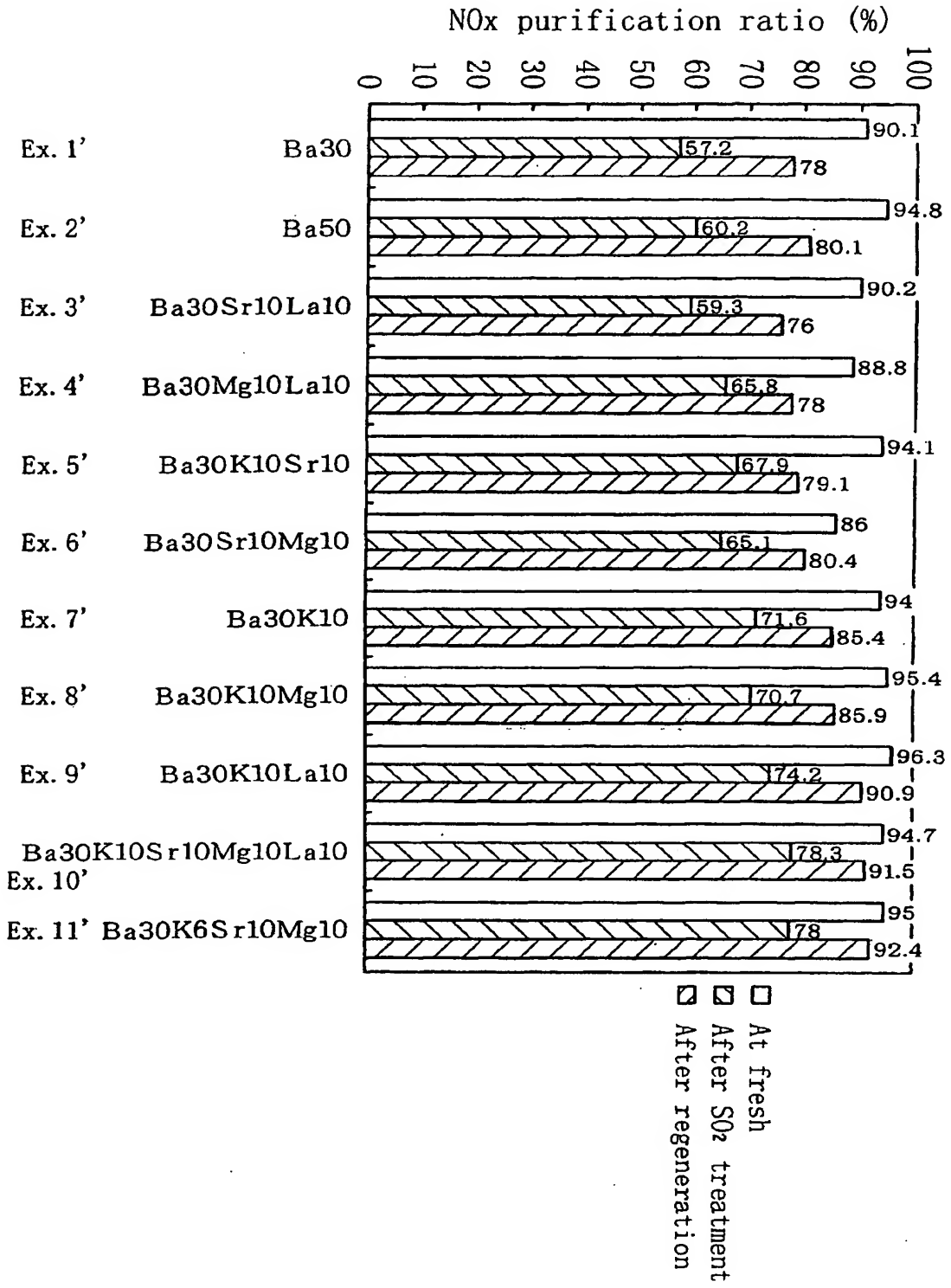

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FIG. 27

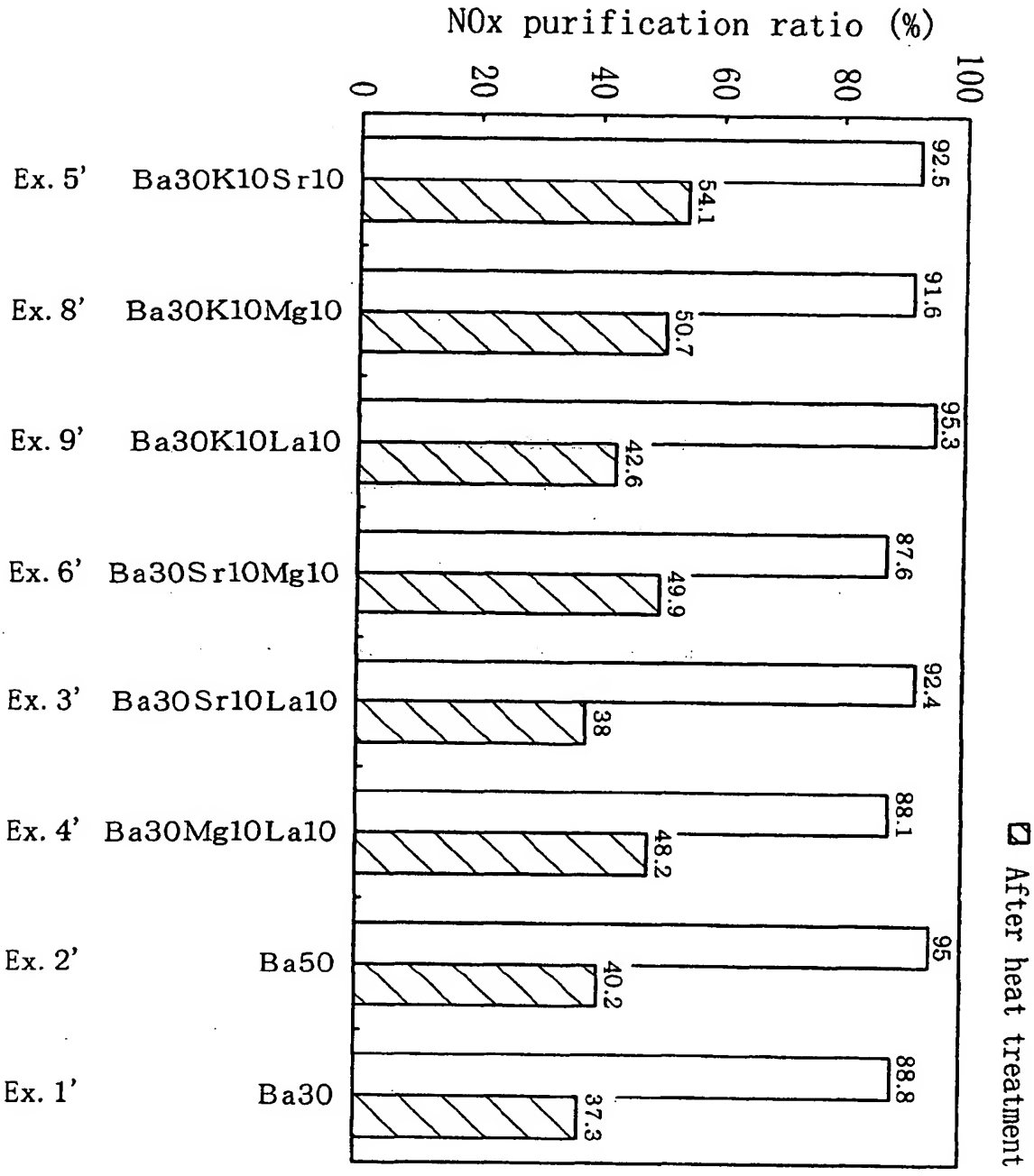
NOx purification ratio (%)
0
20
40
60
80
100
Ex. 5' Ba30K10Sr10
92.5
54.1
Ex. 8' Ba30K10Mg10
91.6
50.7
Ex. 9' Ba30K10La10
95.3
42.6
Ex. 6' Ba30Sr10Mg10
87.6
49.9
Ex. 3' Ba30Sr10La10
92.4
38
Ex. 4' Ba30Mg10La10
88.1
48.2
Ex. 2' Ba50
95
40.2
Ex. 1' Ba30
88.8
37.3
At fresh
After heat treatment

FIG. 28

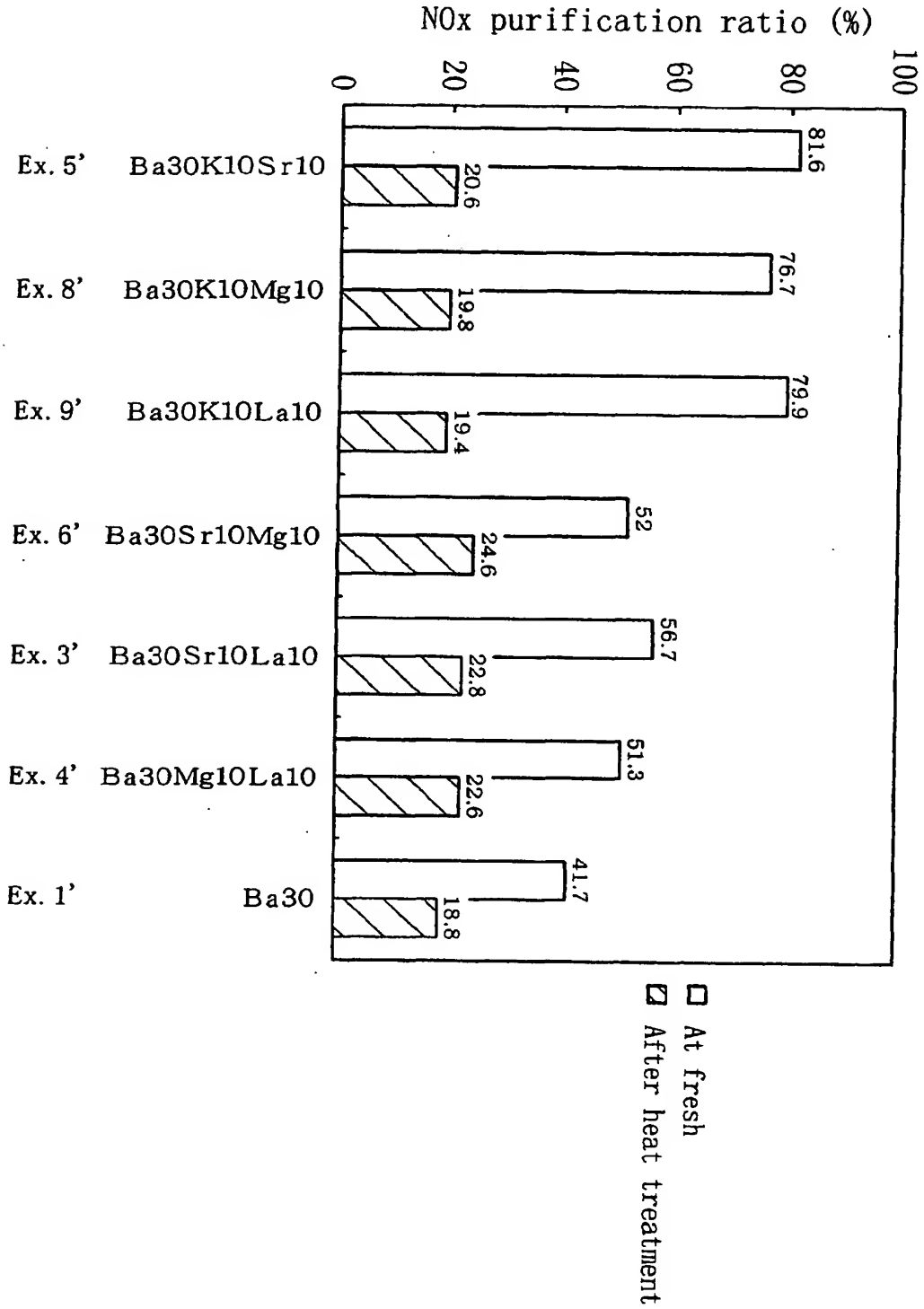

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FIG. 29

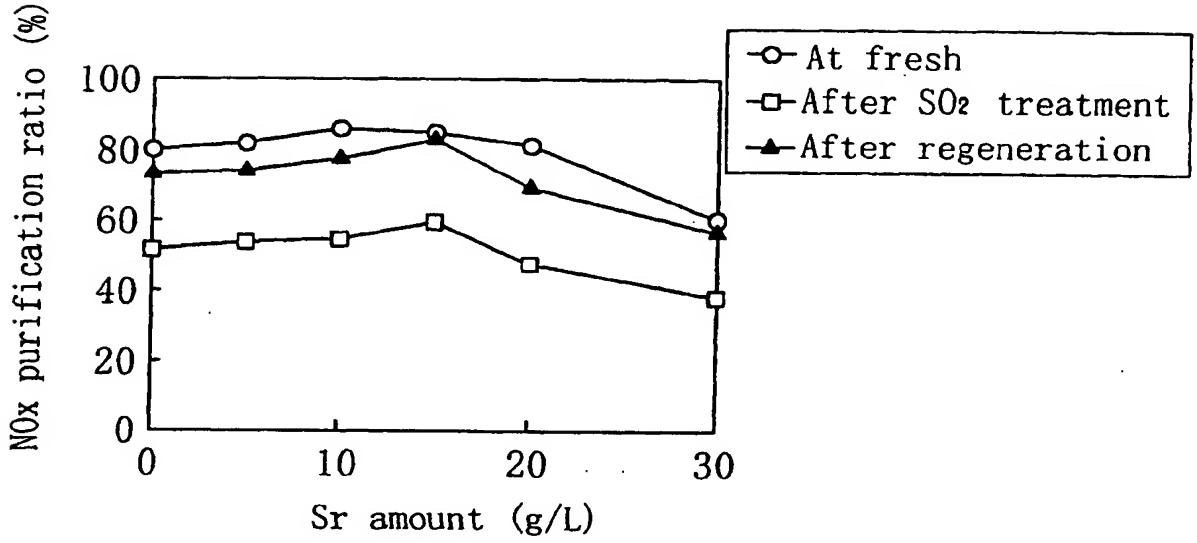
NOx purification ratio (%)
100
80
60
40
20
0
0
10
20
30
Sr amount (g/L)
At fresh
After SO2 treatment
After regeneration

FIG. 30

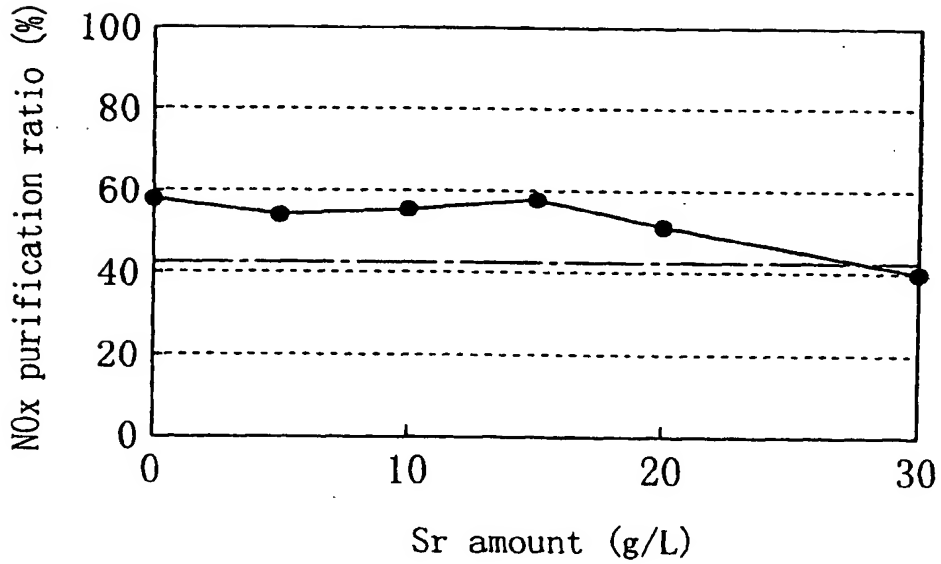
NOx purification ratio (%)
100
80
60
40
20
0
0
10
20
30
Sr amount (g/L)

FIG. 31

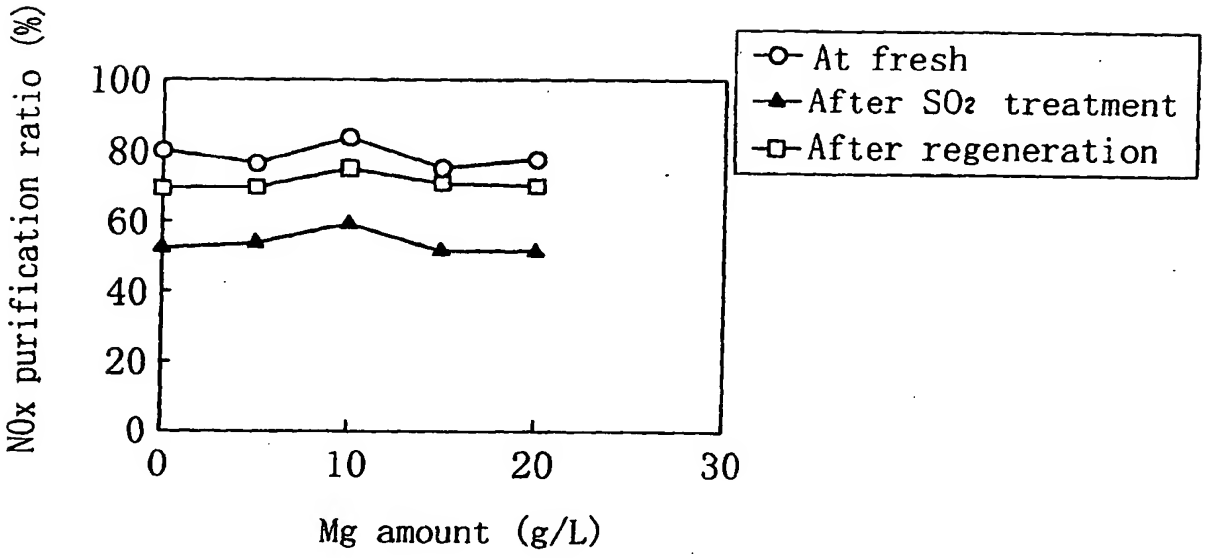

FIG. 32

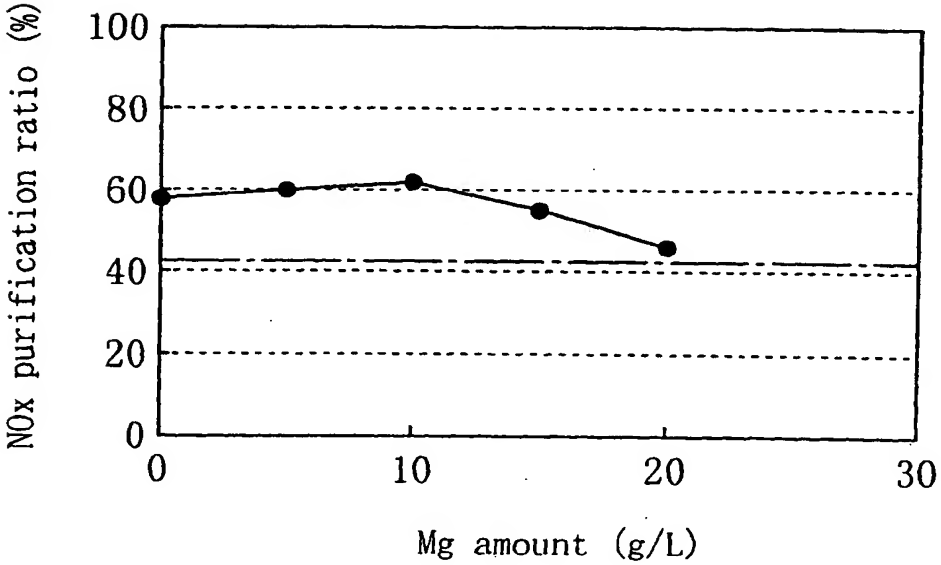

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FIG. 33

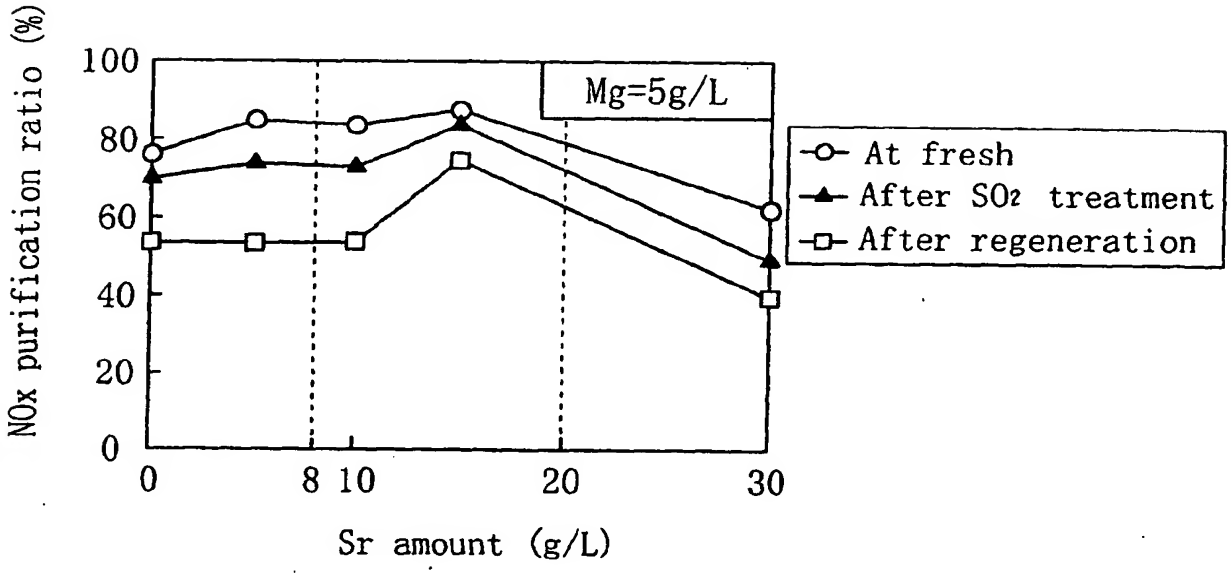

NOx purification ratio (%)
100
80
60
40
20
0
0
8 10
20
30
Sr amount (g/L)
Mg=5g/L
At fresh
After SO2 treatment
After regeneration

FIG. 34

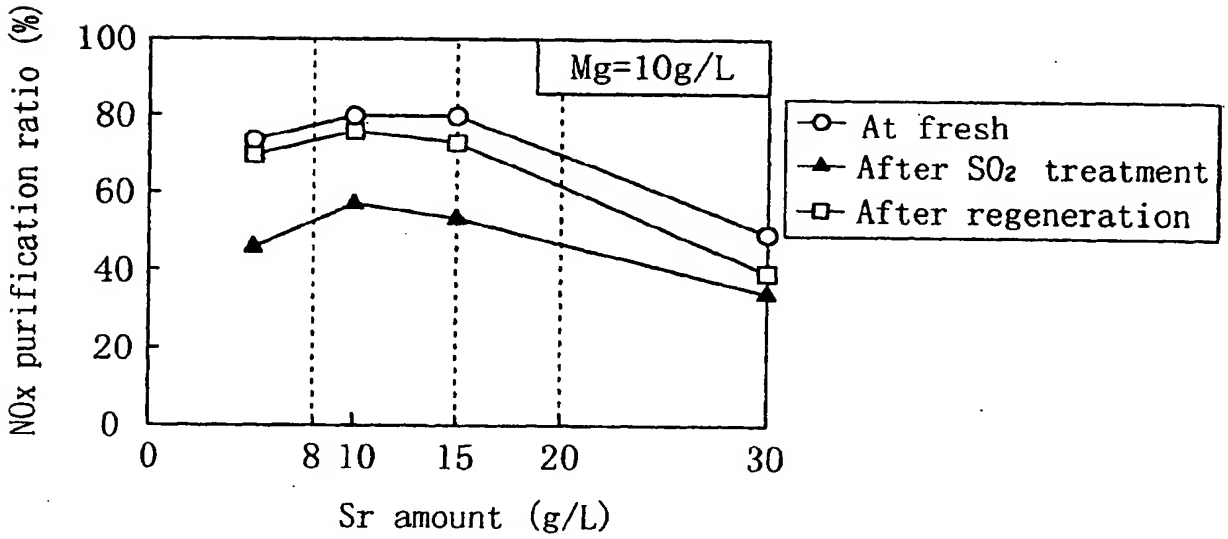

NOx purification ratio (%)
100
80
60
40
20
0
0
8 10
15
20
30
Sr amount (g/L)
Mg=10g/L
At fresh
After SO2 treatment
After regeneration

FIG. 35A

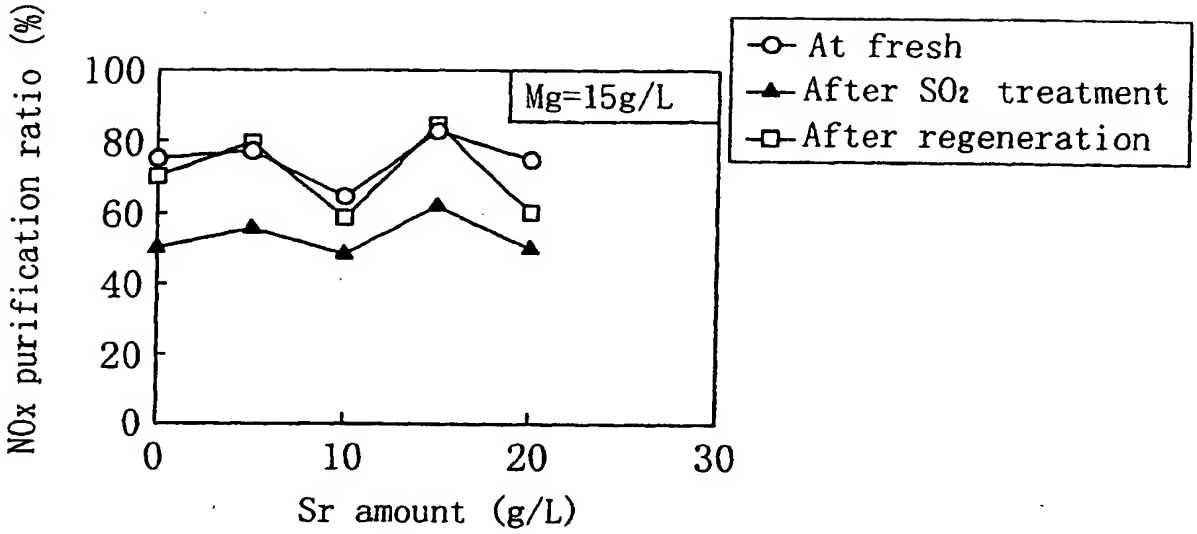
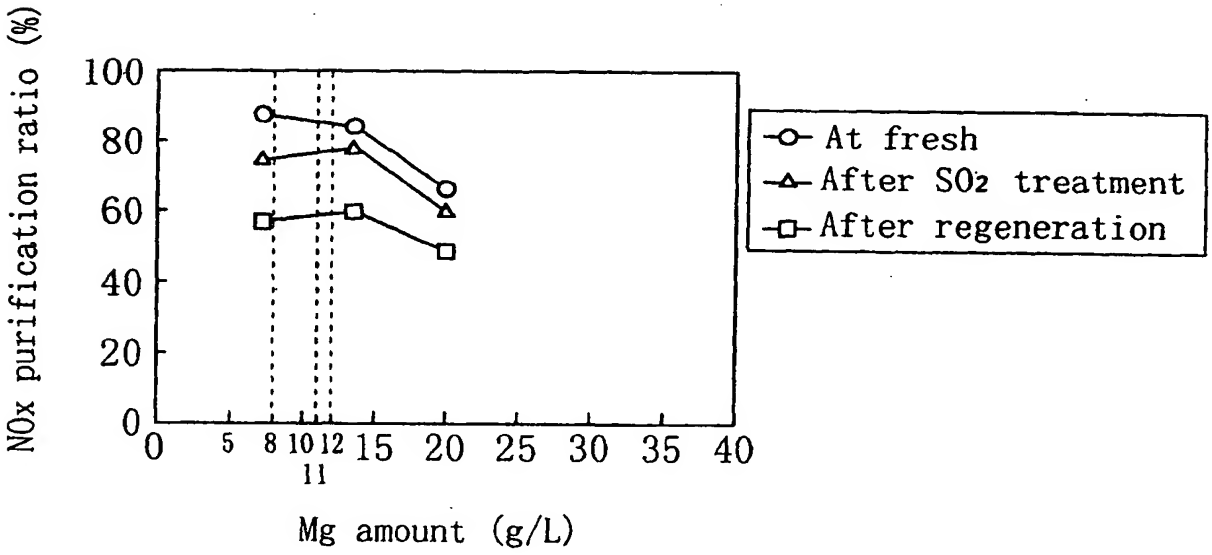


FIG. 35B



NSDOCID: <EP_____1127603A1_I_>

FIG. 36

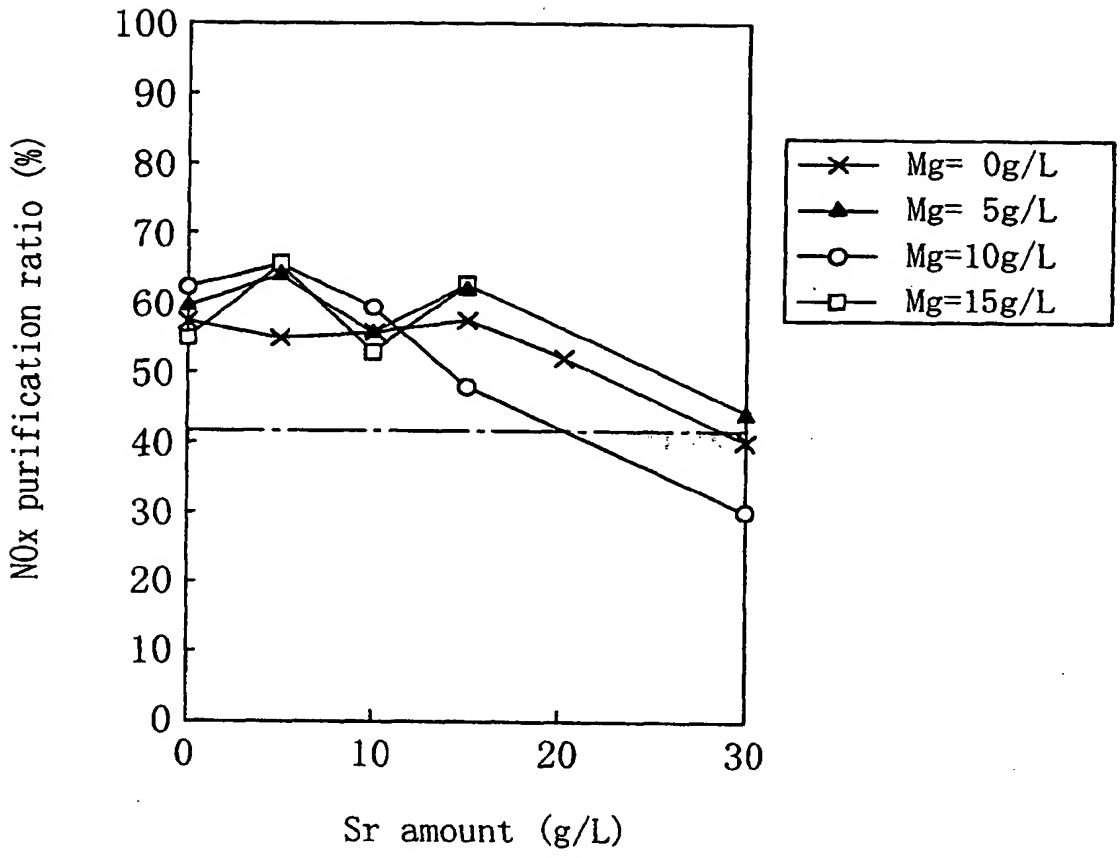
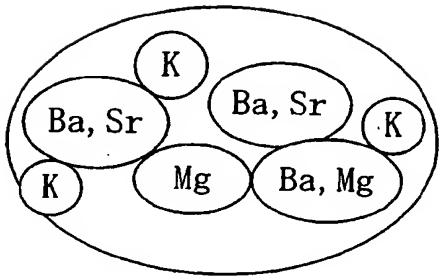

100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
NOx purification ratio (%)
Sr amount (g/L)
Mg= 0g/L
Mg= 5g/L
Mg=10g/L
Mg=15g/L

Fig. 37



SDOCID: <EP_____1127603A1_I_>

Fig. 38

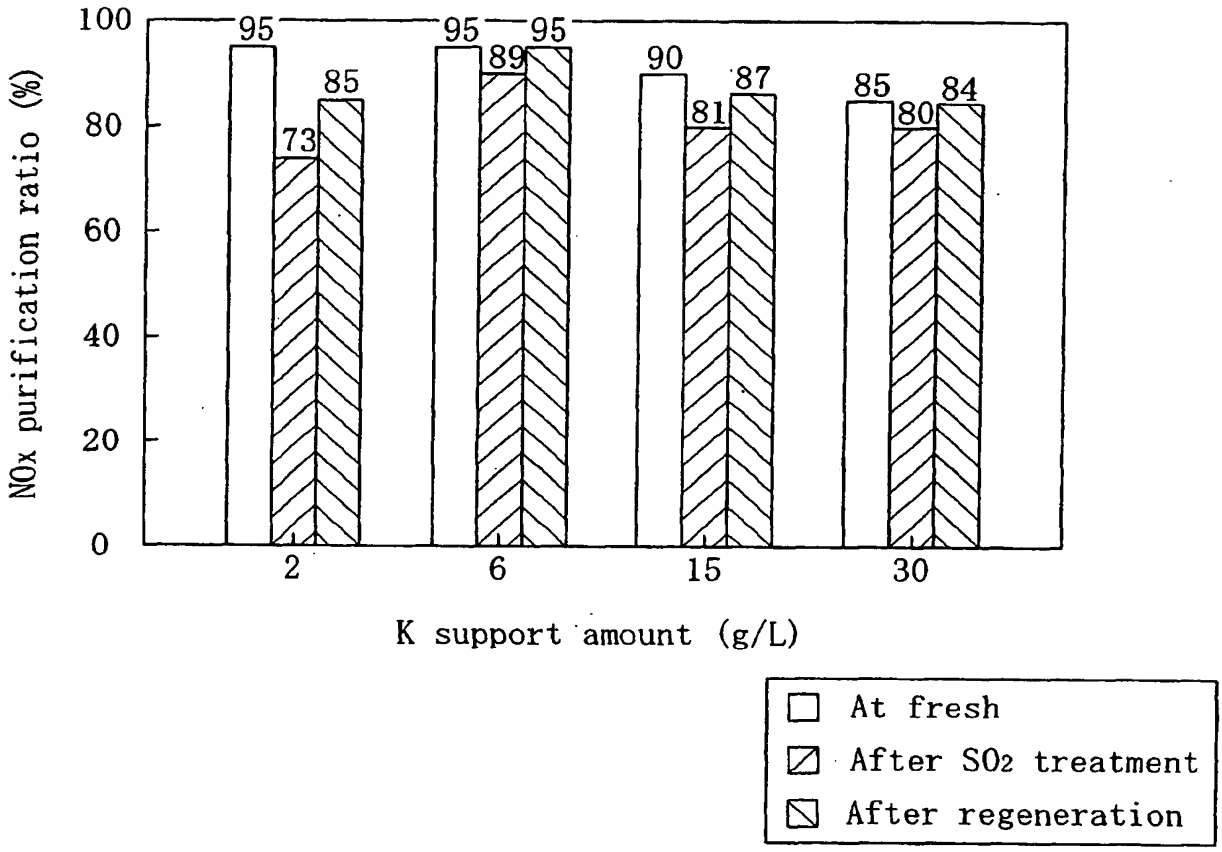

100
80
60
40
20
0
NOx purification ratio (%)
95
73
85
95
89
95
90
81
87
85
80
84
2
6
15
30
K support amount (g/L)
At fresh
After SO2 treatment
After regeneration

Fig. 39

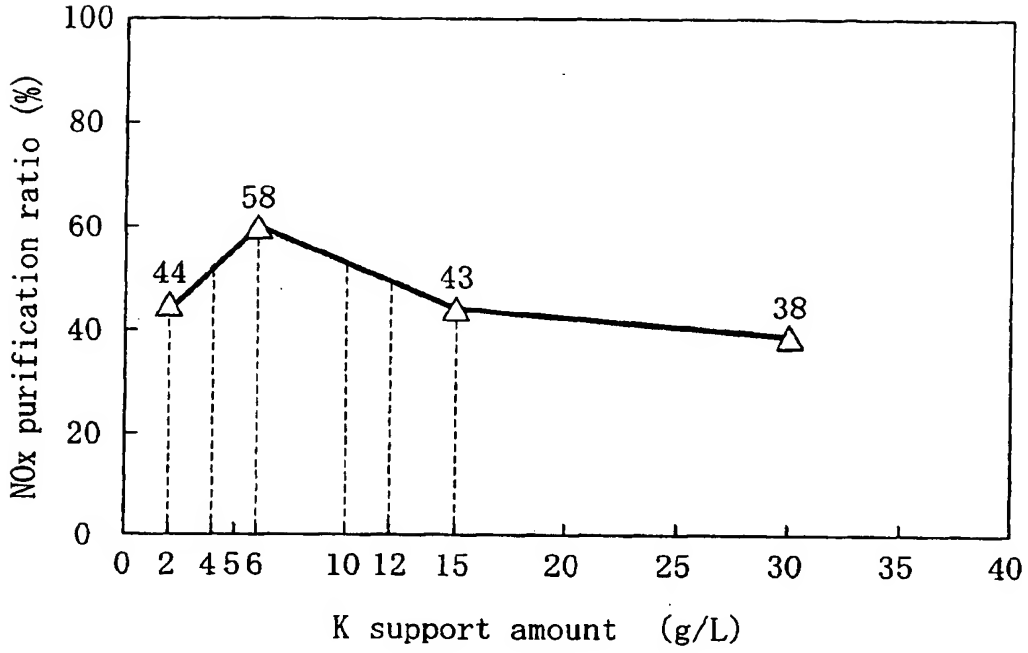


Fig. 40

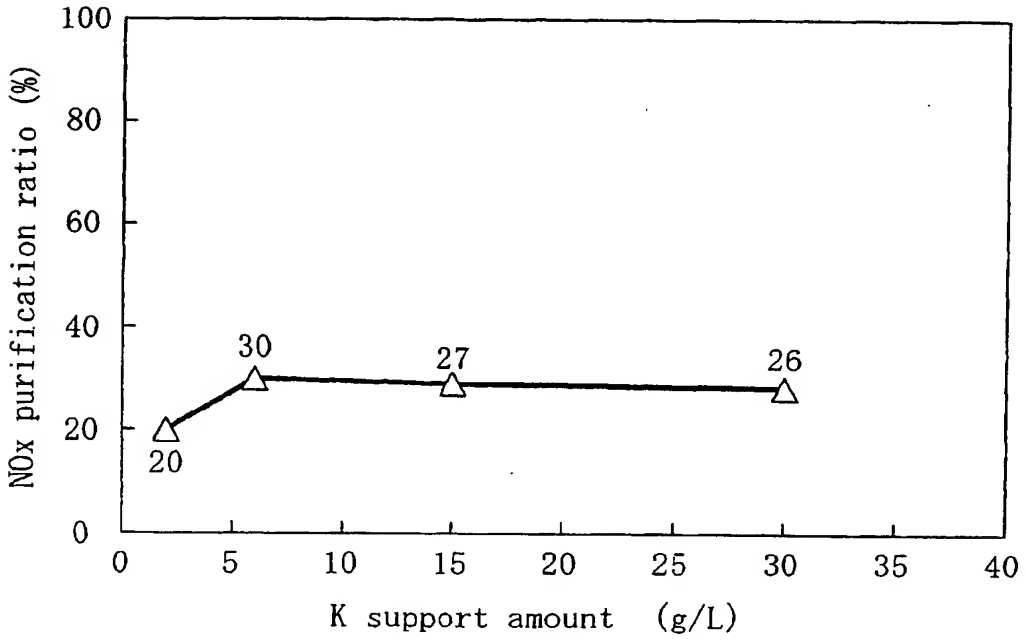


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FIG. 41

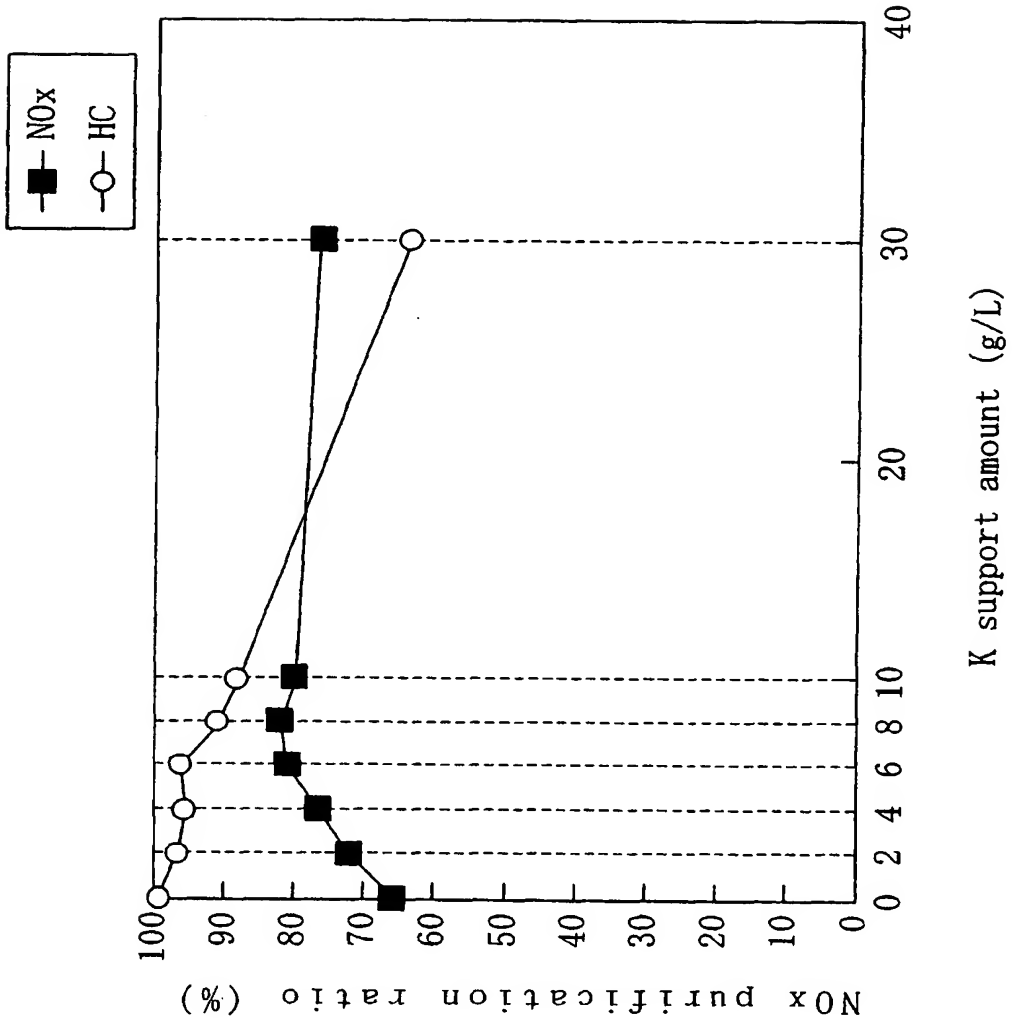
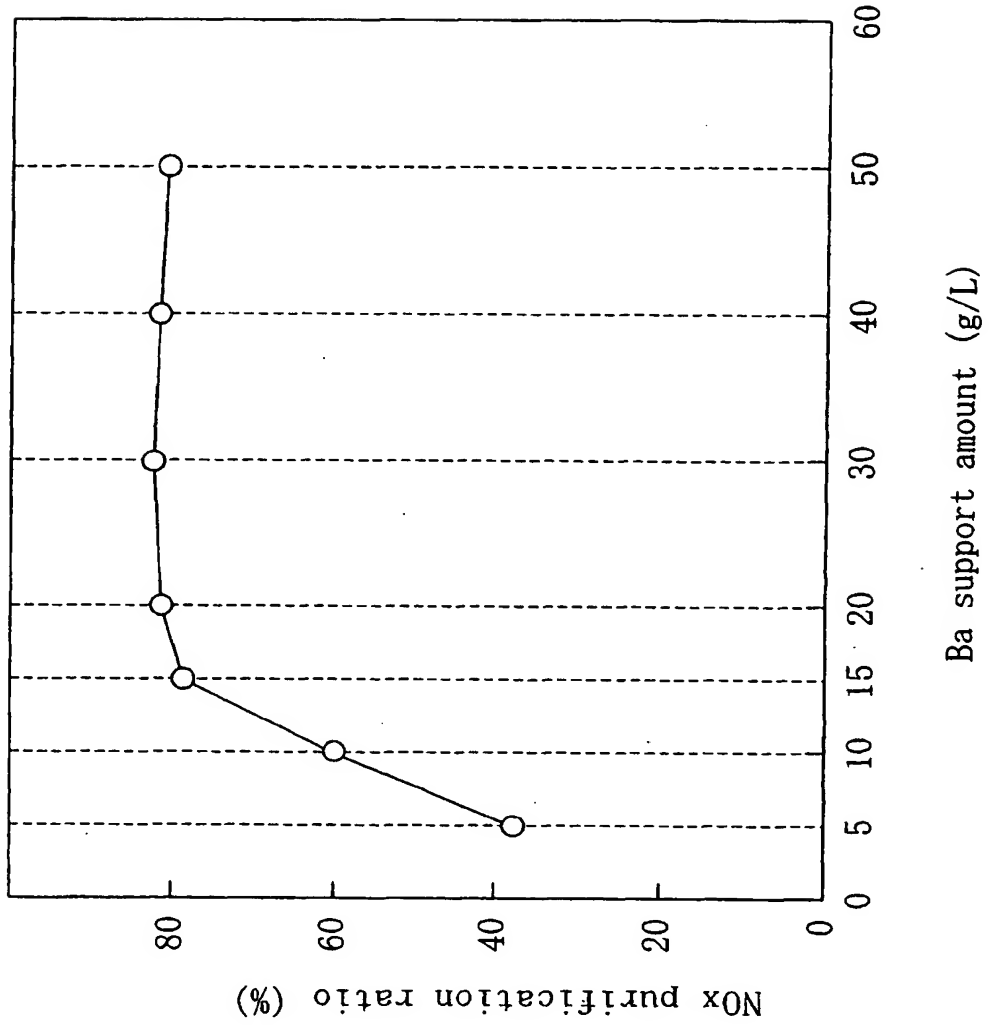

NOx
HC
NOx purification ratio (%)
100
90
80
70
60
50
40
30
20
10
0
0 2 4 6 8 10
20
30
40
K support amount (g/L)

Fig. 42



INSDOCID: <EP_____1127603A1_I_>

Fig. 43

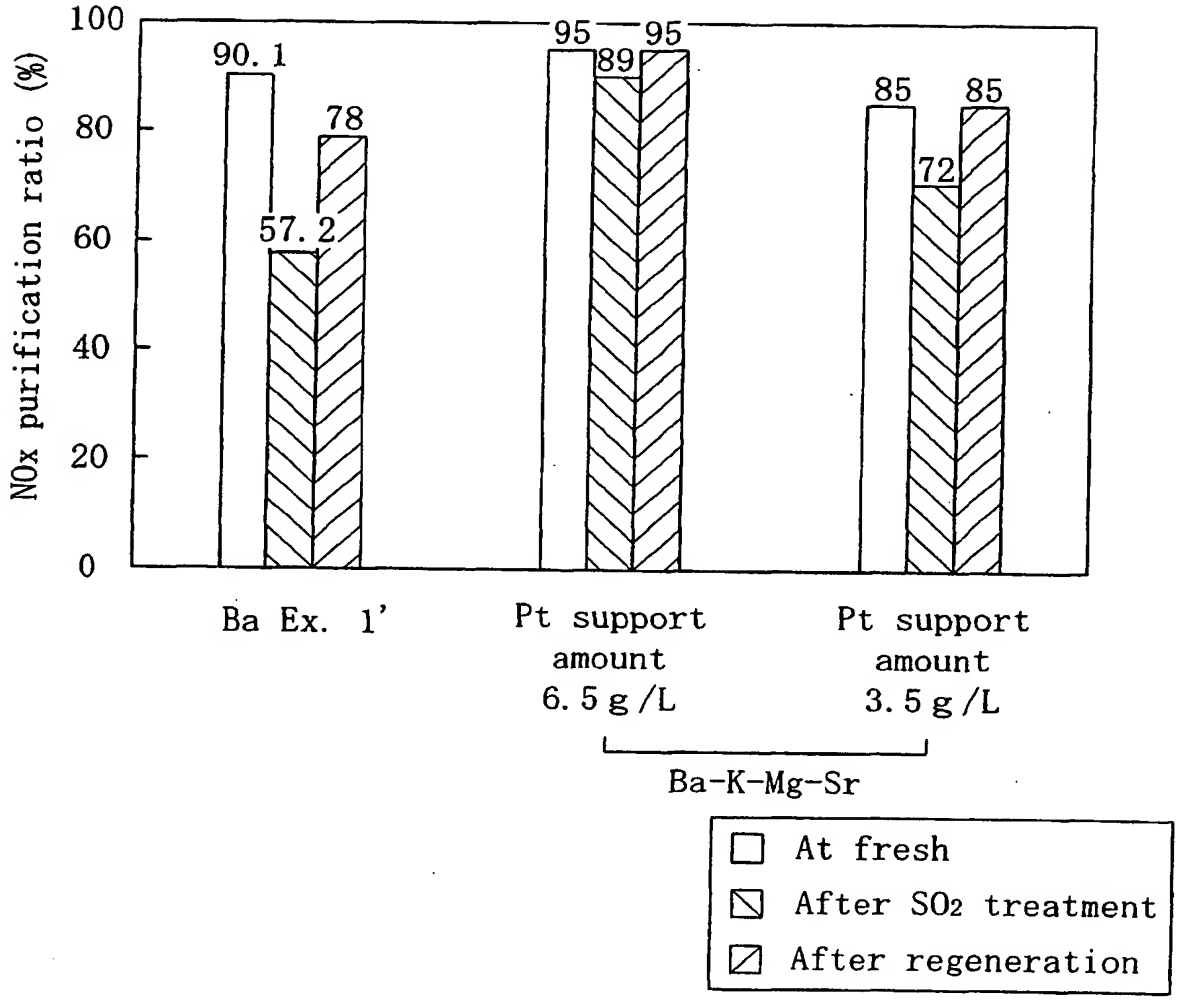

NOx purification ratio (%)
100
80
60
40
20
0
90.1
57.2
78
95
89
95
85
72
85
Ba Ex. 1'
Pt support amount 6.5 g/L
Pt support amount 3.5 g/L
Ba-K-Mg-Sr
At fresh
After SO2 treatment
After regeneration

Fig. 44

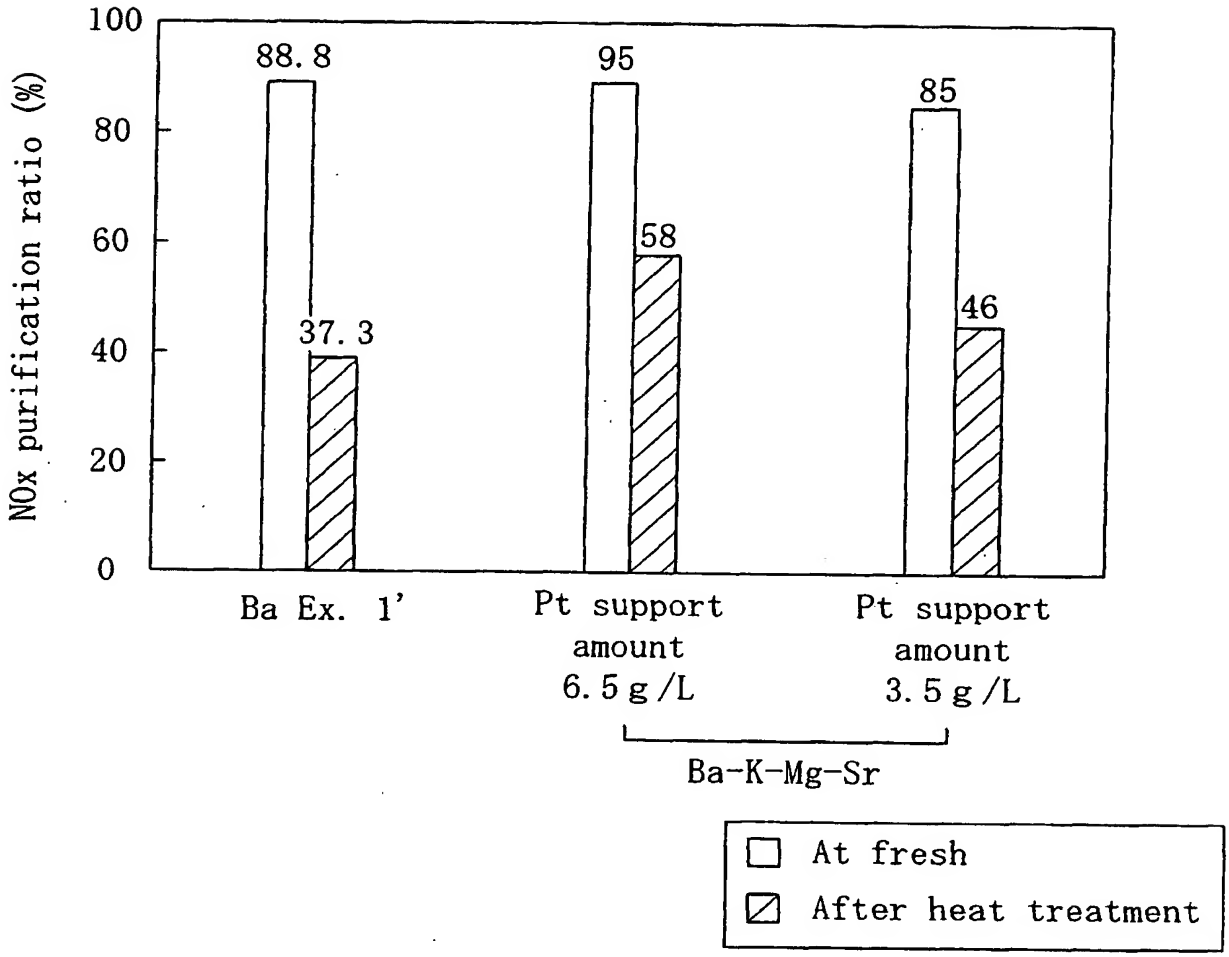


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Fig. 45

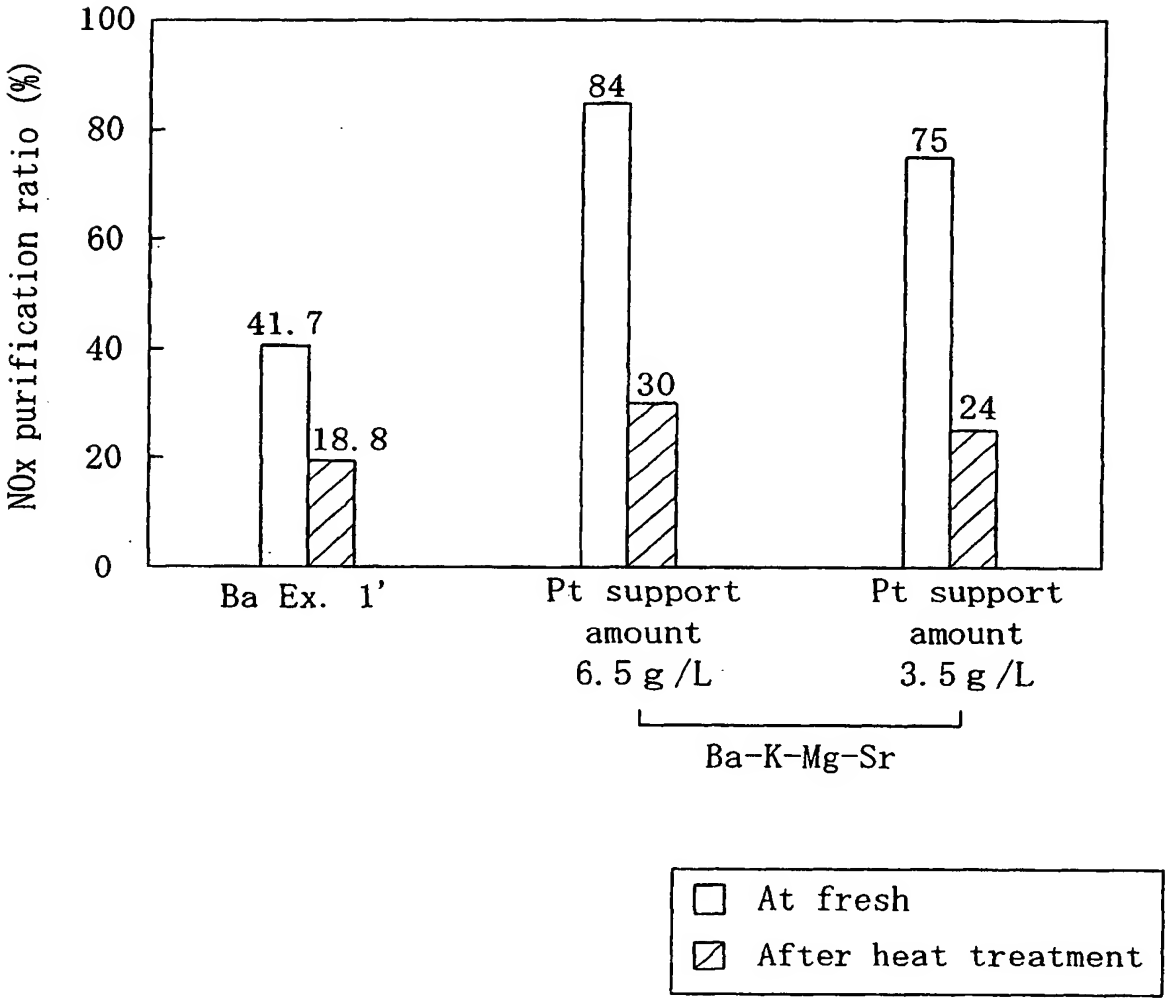
NOx purification ratio (%)
100
80
60
40
20
0
41.7
18.8
84
30
75
24
Ba Ex. 1'
Pt support amount 6.5 g/L
Pt support amount 3.5 g/L
Ba-K-Mg-Sr
At fresh
After heat treatment

Fig. 46

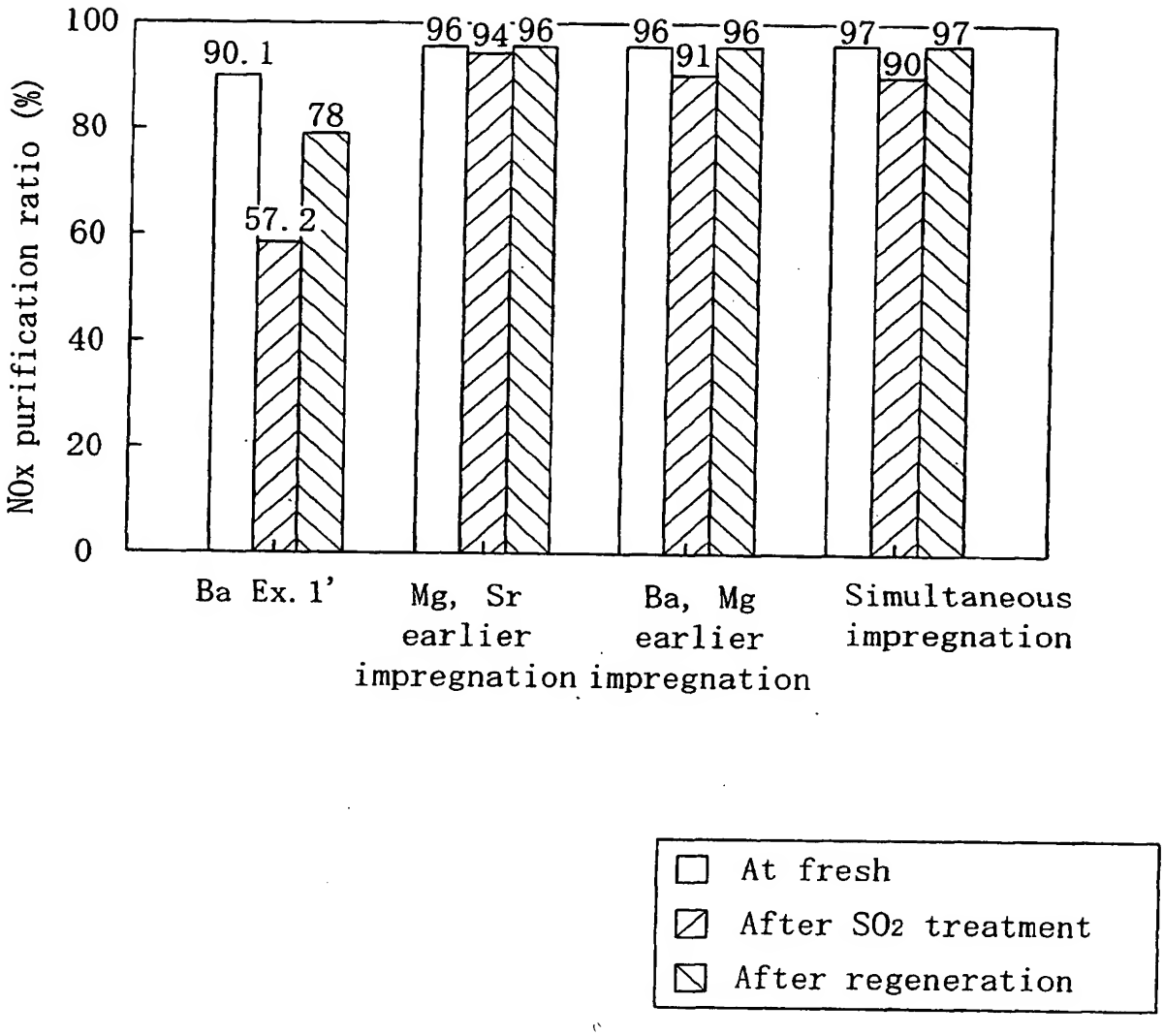

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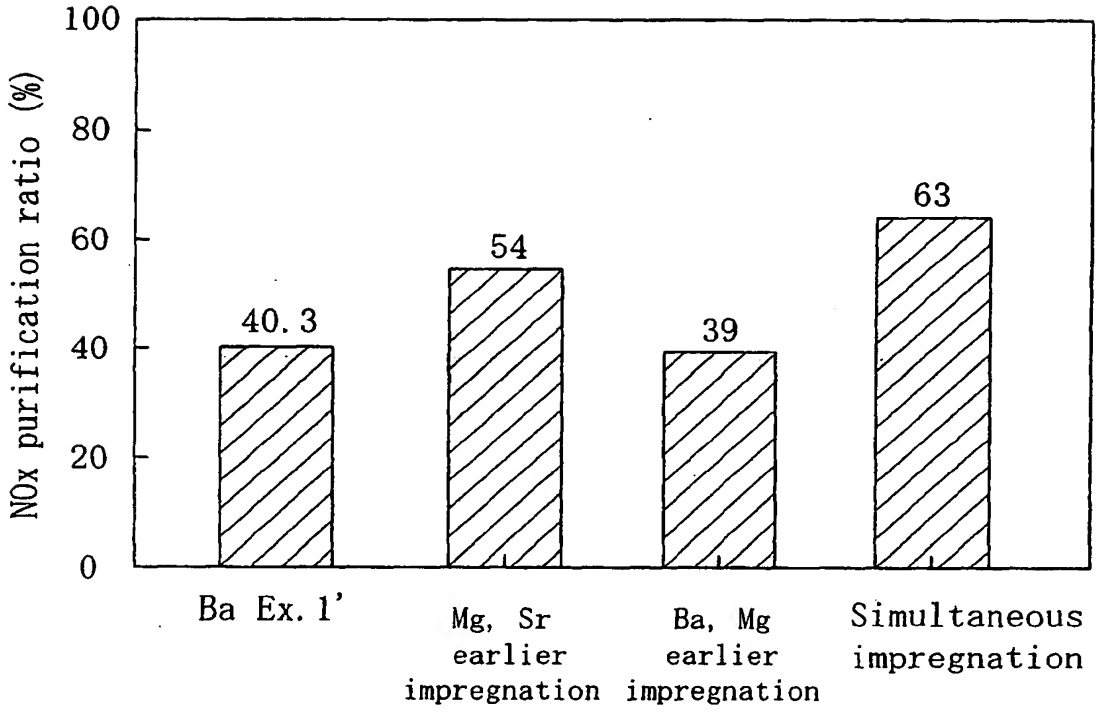
Fig. 47


NOx purification ratio (%)
100
80
60
40
20
0
40.3
54
39
63
Ba Ex. 1'
Mg, Sr earlier impregnation
Ba, Mg earlier impregnation
Simultaneous impregnation

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 10 4294

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B01D
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	9 July 2001	Cubas Alcaraz, J

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